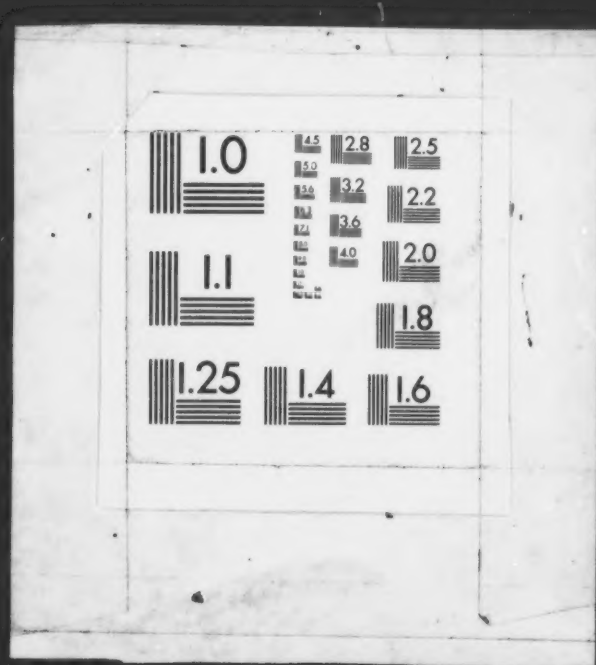


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Determination of Phenols in
Industrial and Municipal Wastewaters

IT Envirosience, Inc., Knoxville, TN

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

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October 1985

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DETERMINATION OF PHENOLS IN
INDUSTRIAL AND MUNICIPAL WASTEWATERS

By

J. R. Florance, J. R. Hall, M. Khare, S. M. Maggio, J. C. Mitchell,
R. A. Solomon, J. R. SoloRio, D. L. Strother, and M. N. Wass

IT Enviroscience
Knoxville, Tennessee 37923

Contract No. 68-03-2625

Project Officer
James J. Lichtenberg
Physical and Chemical Methods Branch
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- o Develop and evaluate methods to measure the presence and concentration of physical, chemical and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- o Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- o Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- o Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

Under authority of Sections 304(h) and 501(a) of the Federal Water Pollution Control Act of 1972 and the Clean Water Act of 1977, the Environmental Protection Agency is required to promulgate guidelines establishing test procedures for the analysis of pollutants. This report represents the state-of-the-art for the measurement of phenols in industrial wastewaters.

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory - Cincinnati

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ABSTRACT

The objective of this report is to present the data and the research carried out to develop an analytical test procedure for the analysis of specific organic toxic substances in effluent wastewaters. The procedure is for the analysis of 11 of the 114 priority or toxic pollutants identified by the EPA as Category 8 -- Phenols.

The procedures consist of several steps, including extraction, concentration, clean up, derivatization with pentafluorobenzyl bromide, and quantification by gas chromatography with electron-capture detection and flame-ionization.

The report describes the work done leading to selection of the procedures and includes data and information on a literature search, sample preservation procedures, elution of the compounds on various gas chromatographic columns, several solvent extraction efficiencies versus pH, stability of compounds in water-soluble solvents, sample extract clean up procedures, and application of the procedures on effluent wastewaters.

The report was submitted in fulfillment of Contract No. 68-03-2625 by IT Enviroscience under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1977 to March 1979, and work was completed as of March 1979.

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LIST OF ABBREVIATIONS

DMCS
φOH
DMP
2-CP
4-CL-3-MP
DCP
TCP
2-NP
4-NP
PCP
4,6-DN-2-MP
2,4-DNP
PFBB

Dimethylchlorosilane
Phenol
2,4-Dimethylphenol
2-Chlorophenol
4-Chloro-3-methylphenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
2-Nitrophenol
4-Nitrophenol
Pentachlorophenol
4,6-Dinitro-2-methylphenol
2,4-Dinitrophenol
Pentafluorobenzyl bromide

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The careful and critical evaluation of IT Enviroscience's work with helpful suggestions by the EPA Project Officer, James P. Lichtenberg, and the EPA Project Coordinator, James Longbottom, is sincerely appreciated and was beneficial to the project.

The cooperation and assistance of Dr. David L. Stalling, Chief Chemist, U.S. Department of Interior, Columbia National Fisheries Research Laboratory, Columbia, Missouri, and Dr. F. K. Kawahara of the EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, in developing a phenol derivatization technique are gratefully acknowledged.

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SECTION 1

INTRODUCTION

The Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) and more recently the Amendments of 1977 (PL 95-217) require in Section 304(h) that the Administrator of the U.S. Environmental Protection Agency promulgate guidelines establishing test procedures for the analysis of the priority pollutants, which are separated into 12 categories. This report covers the research activity required in the method development for one of those categories: Category 8 -- Phenols.

The 11 compounds in Category 8 -- Phenols are phenol, 2,4-dimethylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 4-chloro-3-methylphenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, and 4,6-dinitro-2-methylphenol.

The study includes a literature search from 1960 through 1978, sample preservation studies, evaluation of solvents for liquid-liquid extraction, stability studies of the compounds in water-miscible solvents, and evaluation of sample and extract clean up procedures.

The use of XAD-26 resin as a possible extraction and concentration step for all the priority pollutant phenolics in wastewater was evaluated and compared to liquid-liquid extraction.

The gas chromatographic characteristics data of the category compounds are presented and include information on retention times with various gas chromatography columns at different temperatures, responses to both electron-capture and flame ionization detectors, linearity curves and chemical data for all compounds, and calculated and practical minimum detectable levels.

To enhance the electron-capture response of the phenols, two derivation techniques were investigated with the results described in this report. Pentafluorobenzyl bromide reaction was selected for incorporation in the procedure.

Based on the information gathered in the research program, methods were proposed for Category 8. These proposed methods were then used to develop data on overall compound recoveries in spiked distilled water and wastewater effluent samples.

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CONCLUSIONS AND RECOMMENDATIONS

The results of the preservation study experiments indicate that the samples are best preserved when buffered to a pH of 7 or 10, dechlorinated with 35 mg of sodium thiosulfate per mg/L of Cl_2 per liter of water, exposed to a minimum of light (UV), and stored and shipped at a temperature of 4°C. These procedures should be performed or implemented as soon as possible after the sample is collected. Adjustment of the samples to a pH of 12 and extraction with dichloromethane serves as a preliminary clean up procedure by removing the base/neutral extractables and leaving the phenols in the water.

The extraction of the water samples, with three 60 mL portions dichloromethane per liter, after adjustment to a pH of 2 with 1 N H_2SO_4 was found to give the best overall extraction efficiencies, which ranged from 42 to 100%. The dichloromethane was concentrated in a Kuderna-Danish evaporator with solvent exchange to 2-propanol.

The gas chromatography with flame ionization detection (GC/FID) determination of the underivatized phenols performed best on a 1.25-m-long by 2.0-mm-I.D. glass column packed with 1% SP-1240 DA on 100/120 mesh Supelcoport with temperature programming. This column, however, gave poor resolution of the 2,4-dimethylphenol and 2,4-dichlorophenol peaks.

Gas chromatography with electron-capture (GC/EC) detection of the underivatized phenols yielded four phenols with poor EC response at concentrations lower than 1 mg/L in the solvent: phenol, 2,4-dimethylphenol, 2-chlorophenol, and 4-chloro-3-methylphenol. The SP-1240 DA column with an electron-capture detector using 95% argon -- 5% methane as the carrier gas resulted in poor resolution and peak shape of the two dinitrophenols and pentachlorophenol at less than 1 mg/L compared with those obtained on the same column using a nitrogen carrier gas and an FID detector.

Derivatization of the phenols with chloroacetic anhydride was unsuccessful due to poor reaction efficiencies and significant artifact formation.

The pentafluorobenzyl derivatives of the phenols in 2-propanol were prepared by adding a sufficient quantity of 2% solution of pentabromobenzyl bromide and 18 Crown-6 catalyst in 2-propanol to yield a 60-fold molar excess of the derivatizing agents.

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GC/EC determination of the derivatives was performed on a 2.8-m-long by 2.0-mm-I.D. glass column packed with a 5% OV-17 on 80/100 mesh Chromsorb W-AW-DMCS at 200°C.

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All 11 phenolic derivatives were resolved by this column, with a minimum resolution of 0.95 occurring between the 2,4-dimethylphenol and 2-chlorophenol derivatives.

The response of the free phenols by GC/FID was in general linear. GE/EC response of the free phenols at high mg/L levels was linear; however, at low or sub mg/L levels, linearity data were not obtained for all the compounds because the EC responsiveness was poor or there was excessive tailing.

The pentafluorobenzyl derivatives were linear over a wide range when derivatized at greater than 10 mg/L in the final solution being derivatized and diluted. Studies showed that derivatization of the phenolic mixture at less than 10 mg/L each was not complete or reproducible.

Extracts were concentrated to allow a reproducible derivatization; however, due to the high GC/EC sensitivity of the pentafluorobenzyl bromide derivatives, they could be diluted to reduce the effects of any interferences.

The pentafluorobenzyl derivatization method produced the desired increase in sensitivity for the phenolics in general, but problems may exist in reproducing the derivatives in "real world" samples. To eliminate extraneous peaks in derivatized standard phenolics solutions and possible interference peaks in real world samples, a silica gel clean up procedure was adopted.

The dinitrophenols were found to give such poor derivatization reproducibility that a recommendation was made to quantify them by FID using a SP-1240 DA column.

Three treated industrial effluent samples and a municipal primary effluent sample were analyzed by the complete method with the municipal sample and one industrial wastewater sample showing no Category-8 compounds. One industrial wastewater contained only 2,4-dichlorophenol and 2,4,6-trichlorophenol, while the other industrial wastewater showed eight of the 11 phenols ranging from 25 to 800 µg/L. The method may be applicable to a wide variety of wastewater effluents, but confirmation by a secondary technique, prior sample knowledge, or gas chromatography/mass spectrometry will be required at times.

The accuracy of the complete method based on spiked solutions of distilled deionized water expressed as percent of recovery varied from 30% for 4-nitrophenol to 82% for 2-nitrophenol. The same experiment using spiked municipal wastewater gave an accuracy range from 50% for phenol to 76% for 4-chloro-3-methylphenol. The single operator coefficient of variation ranged from 10% for 2-nitrophenol to 54% for 4,6-dinitro-2-methylphenol in a spiked municipal wastewater sample.

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RECOMMENDATIONS

As noted above, the development of a clean up procedure earlier in the project would have also enabled better quantitative data to be gathered during the extraction and preservation studies of the phenolics.

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Further work should be performed in determining the ideal reaction kinetics of the low level (<10 mg/L) derivatization of phenolics; that is, increased temperature time, catalyst, or reactant concentration may be needed.

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SECTION 3

RESULTS OF LITERATURE SEARCH

The literature review was made to determine the state of the art of analytical instrumentation and techniques utilized in the trace analysis of the 11 phenolics that had been specified by the EPA. The resources of the University of Tennessee Science Library, the Oak Ridge National Laboratory Central Research Library, and IT Enviroscience's own facilities were used for this literature review.

The abstracts listed in Table 1 were searched from the years 1960 to 1979 for key words or subjects including methods of analysis for each of the two categories of compounds, sample collection and preservation methods, concentration techniques, clean up procedures, derivatization techniques and applications of chromatography.

TABLE 1. ABSTRACTS

Analytical Abstracts
Aquatic Sciences Abstracts*
Chemical Abstracts, 1960-1972
Chemical Abstracts Condensates, 1976-1977*
CASIA, 1972-1976*
NTIS*
Pollution Abstracts
Recon Files*

*Computer searches.

Several abstracts were manually searched, but five were searched by computer programs utilizing the key words or subjects mentioned in the last paragraph, along with the topic compound's registry numbers. CASIA is the computer program that searched Chemical Abstracts from 1972 to 1976. More recently, abstracted articles were found when the Chemical Abstracts Condensate program was run. The Recon File is a data bank of key articles that have been compiled by the Oak Ridge National Laboratory Central Research Library for its employees and is available publicly through the University of Tennessee Library.

Table 2 lists the periodicals most often cited by the abstracts. In addition to articles that appeared in these periodicals, numerous books, governmental publications, and minutes of symposia and meetings were cited. Copies of the most pertinent articles were obtained and will be kept on file by IT Enviroscience throughout the lifetime of this project. A complete reference of pertinent publications is given in Section 7.

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Analytical Biochemistry
Analytical Chemistry
Analytical Letters
Bulletin of Environmental Contamination and Toxicology
Environmental Pollution
Environmental Research
Environmental Science and Technology
International Journal of Air and Water Pollution
Journal of Agricultural and Food Chemistry
Journal of American Waterworks Association
Journal of the Association of Official Agricultural Chemists
Journal of the Association of Official Analytical Chemists
Journal of Chromatography
Journal of Chromatographic Science
Journal of Environmental Science and Health
Journal of Industrial Hygiene and Toxicology
Journal of Water Pollution Control Federation
TAPPI
Vom Wasser
Water, Air and Soil Pollution
Water and Sewage Works
Water Pollution Control
Water Research

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Table 3 is a summary of the literature search results for the analysis of specific phenolics.

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Sampling and preservation techniques were most often mentioned in governmental publications, such as reference 269. The recommended procedure, other than refrigeration for preservation of the samples containing phenols, is the addition of copper sulfate followed by acidification to a pH of less than 4 with phosphoric acid.(244) Other methods of preservation were reviewed by Benedek and Najak, but acidification was recommended in most cases.(19)

The common method of removing the phenols from water was liquid-liquid extraction. Dichloromethane, chloroform, and diethylether were the extraction solvents used most often.(70, 143, 177) However, extraction data indicate that methyl isobutyl ketone may be a more efficient solvent.(55) The extraction solvent may be directly injected into a GC with a flame ionization detector for chlorinated solvents or with an electron-capture detector for nonchlorinated extraction solvents. Further concentrations of the phenolics in the organic extract are possible by distillation in a Kuderna-Danish evaporator or by air evaporation of the solvent. The former method is preferred since the loss of the extracted compounds during the concentration step is minimized.

Alternate concentration techniques that were mentioned in the literature are freeze concentration, steam distillation, and carbon adsorption.(9, 28, 225) All these techniques are time consuming and impractical when many samples are processed. Reverse osmosis with an acetate membrane has been used to extract phenols from water, but this technique is practical only on a large scale.(62)

In recent years macroreticular resins, such as Rohm and Haas XAD resins, have been successfully used in concentrating phenols.(46) Reports of recovery range from 80% for pentachlorophenol to 100% for 2,4-dichlorophenol.(34, 41) The method appears to be relatively simple, although it has been reported to suffer from problems of various accuracy and precision.(249) Stepan reports that the best conditions for attaining acceptable accuracy are:

1. Proper cleaning and preparation of resin before packing the columns
2. Constant sample temperature
3. Proper pH adjustment of sample
4. Constant flow rate during elution

Burnham, Chang, and Chriswell successfully utilized a series of pH-adjusted eluants to selectively elute and resolve mixtures of acidic, basic, and neutral compounds.(34, 41, 45) This strongly suggests the possibility of using the technique for clean up as well as for extraction.

When the water extracts required "clean up" to remove potential GC interferences, simple back extraction was sufficient in a few cases to remove acidic interferences.(232) The most widely reported clean up tech-

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TABLE 3. CITATIONS FOUND IN LITERATURE FOR ELEVEN TOPIC PHENOLS

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	Methods Listed	Articles Listed
Total citations		281
Sampling and preservations		14
Preservation techniques	3	
Concentration by liquid-liquid extractions		68
Extraction solvents	24	
Concentration by carbon adsorption		9
Concentration by osmosis/dialysis		7
Concentration by macroreticular resins		19
Clean up		13
Techniques	8	
Analysis by GC		142
GC substrates	82	
Purge/sparge techniques		8
Direct aqueous analysis by GC		13
Analysis of derivatives by GC		60
Derivation chemicals	18	
Analysis by LC		21

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nique is column chromatography with silica gel, Florisil, alumina, or magnesium carbonate in which petroleum ether or dichloromethane is used as the eluant.(48) Thin-layer chromatography and liquid chromatography are used less frequently.(39, 239)

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It was very surprising to find that many different GC columns were used for the separation and determination of phenolic compounds, which only points out the difficulty encountered when mixtures of phenols are being analyzed. While some of the reported columns were used for the separation and analysis of derivatives of the phenols, most were used for direct analysis. No particular columns stood out although the substrate Carbowax-20M was reported in seven articles while SE-30 and dinonylphthalate were mentioned in five.(13, 99, 208) During the period of this work Supelco, Inc., made commercially available their product SP-1240 DA, which provides the best separation on packed columns reported to date for these 11 compounds.

The use of both flame ionization and electron-capture detectors was reported in the literature. Generally, the FID-gas chromatographic analyses of the phenols appeared to be relatively insensitive and limited to simple mixtures due to interferences. In most cases EC-gas chromatographic analyses of derivatives of phenols provided greater sensitivity. Separation of derivatives of phenols was more complete than that for the compounds not derivatized.

Since phenols often "tail" on most GC columns and sometimes have poor response to FID or EC detectors, their derivatization preceding GC analysis is advisable. Eighteen different derivation reagents were mentioned for the phenols in the literature. Bis(trimethylsilyl)acetamide and diazomethane were the two most often reported.(22, 246) However, neither one reacts quantitatively with all phenols.

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PHENOLS

INTRODUCTION

The 114 organic compounds in 12 categories have been designated as priority pollutants by the EPA. This study was undertaken to develop methodologies for the quantification of the 11 Category-8 phenols: phenol, 2,4-dimethylphenol, 2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol, 4,6-dinitro-2-methylphenol, and 2,4-dinitrophenol.

The technical objectives of this project included the determination of a sample preservation scheme to minimize compound loss, the derivation of an efficient extraction technique for recovering and concentrating the compounds from water, the establishment of a reliable and linear gas chromatographic method applicable to all 11 compounds, the determination of the stability of the compound when dissolved in water-miscible solvents, the development of a suitable sample clean up procedure, the application of the final analytical method with a clean up procedure to effluent wastewater samples, the utilization of spiked aliquots of the wastewater sample taken through the complete method to gather accuracy and precision data, and the selection of the best derivatization procedure that most efficiently would resolve the compounds in low-ppb ($\mu\text{g/L}$) ranges.

The experimental data indicated that the samples were best preserved when buffered to a pH of 7 to 10, dechlorinated with 35 mg of sodium thiosulfate per mg/L of Cl_2 per liter of water, exposed to a minimum of light (UV), and stored and shipped at a temperature of 4°C . These procedures should be performed or implemented as soon as possible after the sample has been collected.

Extraction of the samples, which were adjusted to pH 2 with 1 N H_2SO_4 , was performed with three 60 mL portions of dichloromethane. The dichloromethane was concentrated and solvent-substituted with 2-propanol.

GC/FID analysis of the underivatized phenols on a 1.25-m-long by 2.0-mm-I.D. glass column packed with 1% SP-1240 DA on 80/100 Supelcoport was successful, with the poorest separation occurring between the 2,4-dimethylphenol and 2,4-dichlorophenol peaks. With GC/EC analysis, however, four phenols yielded little electron-capture (EC) response at concentrations lower than 1 mg/L, and the tailing of the dinitrophenols at or below 1 mg/L prevented their quantification and that of the pentachlorophenol. Derivatization of the phenols with chloroacetic anhydride was

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unsuccessful, due to poor reaction efficiencies and significant artifact formation.

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The pentafluorobenzyl bromide (PFBB) derivatives of the phenols in 2-propanol (IPA) were prepared by adding a sufficient quantity of a 2% solution of pentafluorobenzyl bromide and 18 Crown-6 catalyst in 2-propanol to yield a 60 fold molar excess of the derivatizing agents. GC/EC analysis of the derivatives was performed on a 5% OV-17 on 80/100 mesh Chromosorb W-AW-DMCS column, 2.8-m-long by 2.0 mm in inside diameter, at 200°C. All 11 phenol derivatives were resolved by this column, with the minimum resolution of 0.95 occurring between the 2,4-dimethylphenol and 2-chlorophenol derivatives.

In general, the response and linearity of the phenols by GC/FID and the pentafluorobenzyl bromide derivatives by both GC/FID and GC/EC analysis were linear. GC/EC analysis of the free phenols for response and linearity data at low levels was not performed because of poor EC response or excessive tailing.

The clean up procedure produced the desired increase in sensitivity. Problems reproducing the derivatives in real world samples were successfully resolved by using a silica gel clean up scheme.

MATERIALS AND METHODS OF PREPARATION

Chemicals

The 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2-nitrophenol, 4,6-dinitro-2-methylphenol and the derivatizing agent chloroacetic anhydride were obtained from Eastman Kodak Company; the 2-chlorophenol and 2,4-dichlorophenol from Chem Service; the 2,4,6-trichlorophenol, pentachlorophenol, 2,4-dinitrophenol and the derivatizing reagents α -bromo-2,3,4,5,6-pentafluorotoluene (pentafluorobenzyl bromide) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18 Crown-6 catalyst) from Tridom Chemicals; and the 4-nitrophenol and phenol were purchased from Fisher Scientific. Normal laboratory reagents such as sodium sulfate, sulfuric acid, potassium carbonate, hydrochloric acid, potassium chloride, potassium dibasic phosphate, sodium hydroxide, sodium bicarbonate, and sodium thiosulfate were ACS grade and were also obtained from Fisher Scientific. Burdick and Jackson distilled in glass (pesticide grade) hexane, dichloromethane, 2-propanol, petroleum ether, and 2-butanone were purchased from Bodman Chemicals and used without redistillation. Prepurified nitrogen, zero grade hydrogen, and 95% argon--5% methane were obtained from the Linde Division of Union Carbide. Gas chromatography column packings were acquired from Supelco, Inc.

Water Purification

Water of a very high purity is of the utmost importance in these experiments; therefore, a high quality purification system was utilized. Distilled, deionized water was prepared by filtering tap water through a

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Carborundum Company tube filtration unit, followed by elution through a Barnstead D8904 organic removal column, a Barnstead D8901 high capacity ion exchange column, and finally a Barnstead D8902 ultrapure ion exchange column. The effluent water was then distilled in a Corning megapure distillation unit that had been modified to prevent all surfaces other than Teflon[®] and glass from contacting the water. All the plumbing and storage containers throughout the system were made of Teflon or glass.

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Gas Chromatography Column Preparation

Glass wool treated with dimethylchlorosilane (DMCS) was inserted into the detector end of a coiled glass column, which was then attached by flexible tubing to a water aspiration vacuum source. The desired packing material was then added to the other end of the column while suction was applied. After the column was filled, a vibrator was used in conjunction with the suction to provide a uniformly packed column. Additional packing material was added as before, if the previous treatment had reduced the volume of the packing material. Another piece of glass wool was inserted in the injector end of the column, and the column fitted with quarter inch Swagelok fittings with Supeltex M-1 ferrules and attached to the injector of the gas chromatograph. M-2 Vespel ferrules may "freeze" onto the chromatograph fittings leading to column breakage. The columns were conditioned at ambient temperature for 30 minutes followed by a 1°C/min program to a temperature of 250°C and held there overnight.

Apparatus

Kuderna-Danish evaporators were prepared by Lab Glass, Vineland, New Jersey. Glass chromatography columns were obtained from Supelco, Inc. The remaining glassware used in this study was ordered from Fisher Scientific.

Gas chromatographic determinations were performed on an HP 5713A gas chromatograph equipped with a ⁶³Ni electron-capture detector and an HP 5702A gas chromatograph equipped with a flame ionization detector. Chromatograms were recorded on either an HP 3380A or an HP 3380S recording integrator.

EXPERIMENTAL

Gas Chromatography

A gas chromatography/flame ionization detector (GC/FID) method was developed to provide separation of the 11 Category-8 compounds. Table 4 lists the columns evaluated for separation of the phenols. The operating conditions are listed in Table 5.

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TABLE 4. GC COLUMNS EVALUATED FOR CATEGORY 8 BY FID

GC Column No.	Packing	Description
1	Carbowax 20M-TPA	10% Carbowax 20M-TPA on 80/100 mesh Chrom AW; 3.0 m X 2.0 mm I.D. glass
2	Tenax GC	Tenax GC 60/80 mesh; 0.5 m X 2.0 mm I.D. glass
3	SP-1000	1% SP-1000 on 80/100 mesh Carbopak C; 2.0 m X 2.0 mm I.D. glass
4	LAC-2-R-446 + H_3PO_4	2.5% LAC-2-R-446 and 0.2% H_3PO_4 on 100/120 mesh Gas Chrom Q; 2.5 m X 2.0 mm I.D. glass
5	R-1574	1% R-1574 on 100/120 mesh Supelcoport; 1.25 m X 2.0 mm I.D. glass
6	SP-1240 DA	SP-1240 DA on 80/100 Supelcoport; 1.25 m X 2.0 mm I.D. glass

TABLE 5. GC CONDITIONS FOR CATEGORY 8 BY FID

FID temperature, °C	260
Injector temperature, °C	240
Oven temperature, °C	100 and 150
Carrier gas	Nitrogen
Carrier gas flow rate, cc/min	30

Although gas chromatography columns 1 through 5 were evaluated for several conditions, they did not provide the desired separation of the 11 compounds, particularly the dinitrophenols, which were not resolved by any of the five columns. Columns 1, 3, 4, and 5 were found suitable for analyzing the other nine phenols. The Tenax GC column (No. 2) adsorbed the nitrophenols, and produced many artifact peaks not useful for this analysis. Column 6, 1.25 m long by 2 mm in internal diameter, 1% SP-1240 DA on 80/100 mesh Supelcoport, provided the best overall separation of the columns evaluated. The dinitrophenols were well resolved, but the separation of the 2,4-dimethylphenol and the 2,4-dichlorophenol peaks was incomplete (Figs. 1 and 2). The analysis temperature and retention for each compound on the SP-1240 DA column are listed in Table 6.

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- A. 2 - CHLOROPHENOL.
B. 2 - NITROPHENOL.
C. PHENOL
D. 2,4 - DIMETHYLPHENOL
E. 2,4 - DICHLOROPHENOL
F. 2,4,6 - TRICHLOROPHENOL
G. 4 - CHLORO -3- METHYLPHENOL

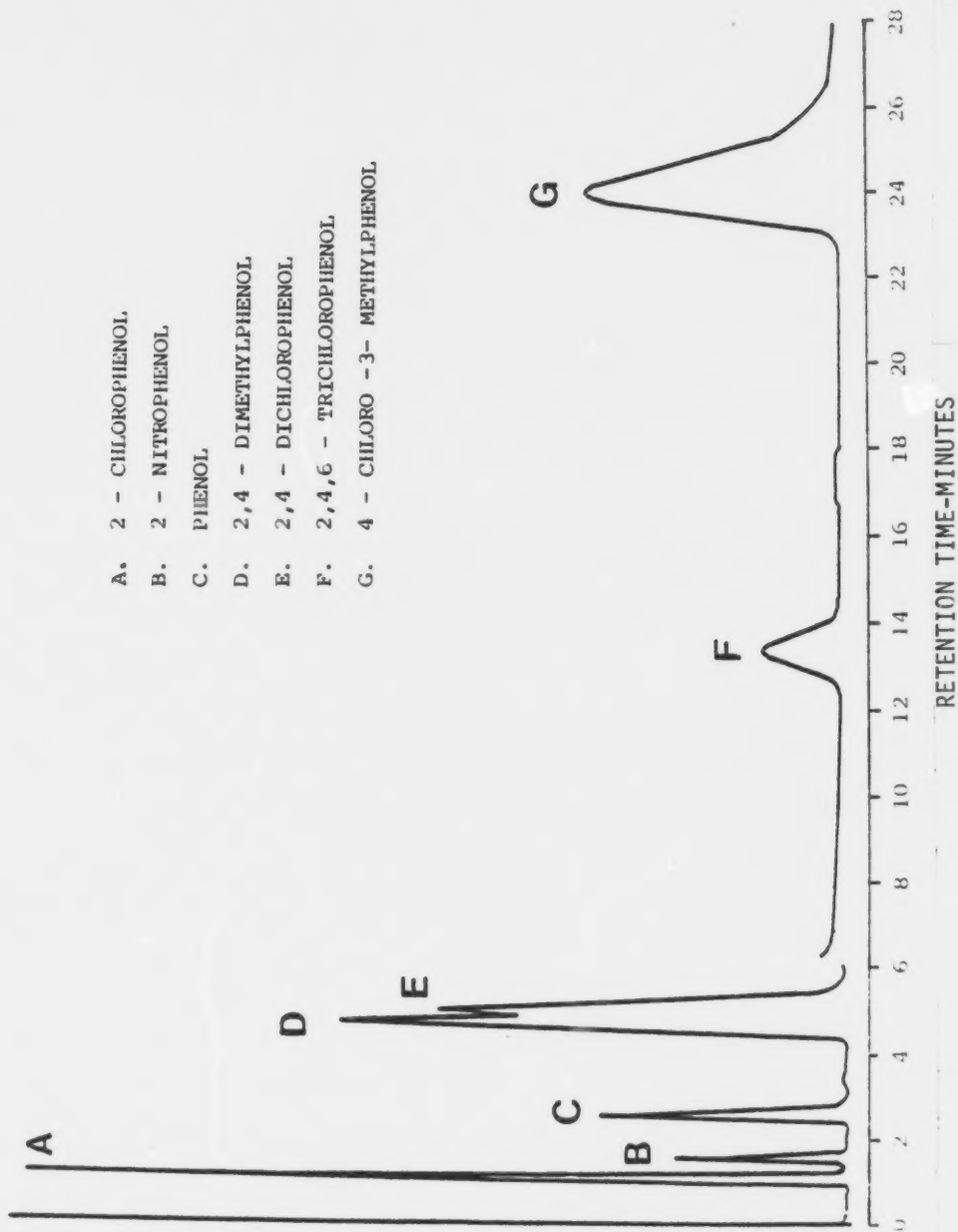


Figure 1. FID Gas Chromatography of Phenols on SP-1240DA at 100°C

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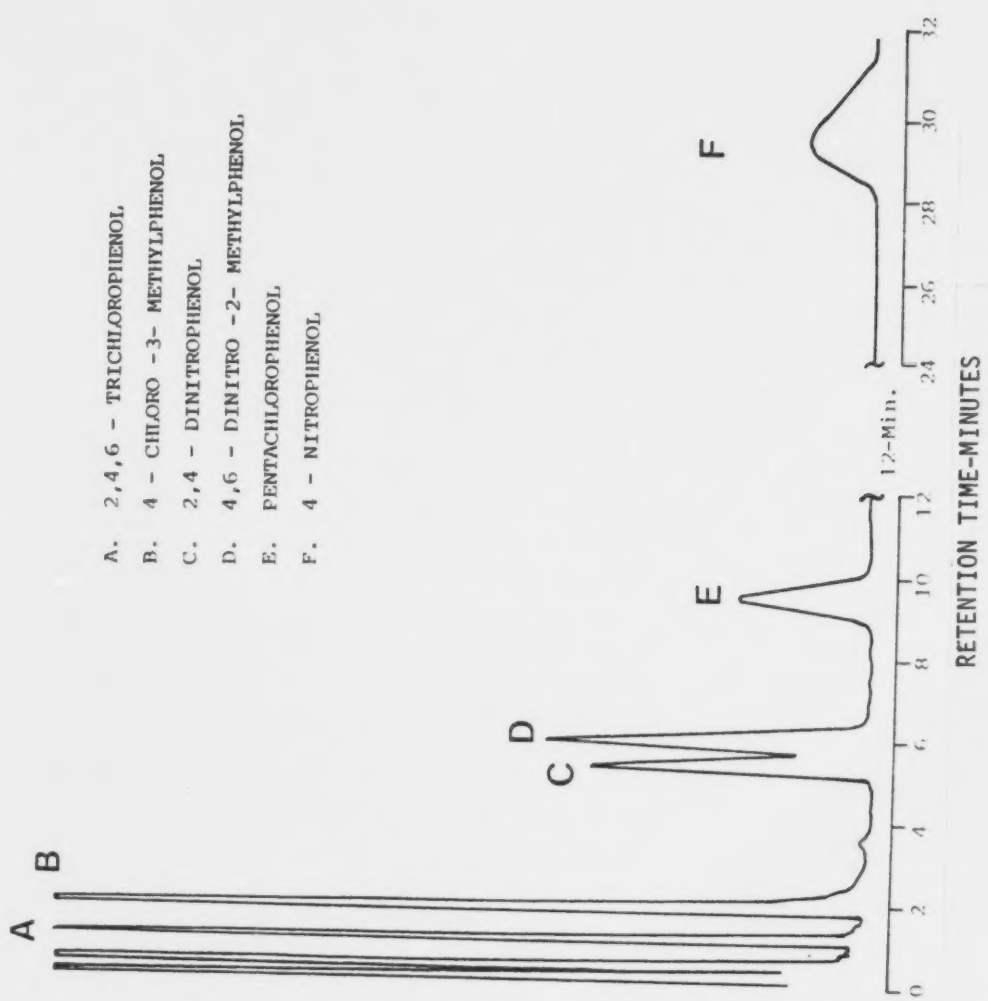


Figure 2. FID Gas Chromatography of Phenols on SP-1240DA at 150°C

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TABLE 6. GC RETENTION TIMES AND
ANALYSIS TEMPERATURES OF CATEGORY 8 BY FID: SP-1240 DA

Compound	Analysis Temperature (°C)	Retention Time (min)
2-CP	100	1.2
2-NP	100	1.6
φOH	100	2.6
DMP	100	4.8
DCP	100	5.1
TCP	100	13.4
4-Cl-3-MP	100	24.0
2,4-DNP	150	5.5
4,6-DN-2-MP	150	6.1
PCP	150	9.5
4-NP	150	29.5

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The GC/FID column of choice (1% SP-1240 DA) was then adapted for GC/EC analyses of the Category-8 phenols. The conditions used in the analyses are listed in Table 7. A flow rate of 30 cc/min of the GC/EC carrier gas, argon/methane, yielded much longer retention times than did the 30 cc/min of nitrogen used for GC/FID analysis. For example, 1,4-dichlorophenol eluted at 5.1 minutes with nitrogen carrier and 8.5 minutes with argon/methane.

TABLE 7. GC CONDITIONS FOR CATEGORY 8 BY EC: SP-1240 DA

EC detector temperature, °C	300
Injector temperature, °C	250
Oven temperature, °C	100 and 150
Carrier gas	95% Argon/5% Methane
Carrier gas flow rate, cc/min	30

Seven of the phenols were detectable by electron capture. However, the other four phenols, 4-chloro-3-methylphenol, 2,4-dimethylphenol, 2-chlorophenol, and phenol, produced very little response at concentrations lower than approximately 1 mg/L. In addition, the dinitrophenol peaks began to merge with each other at the 0.1 to 1.0 mg/L level.

During the course of this study, it was ascertained that the 11 phenols could be separated in a single GC/FID run on SP-1240 DA under temperature programmed condition. Table 8 lists the conditions and retention times for the phenols. Figure 3 is a copy of a typical chromatogram.

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COLUMN: 1 $\frac{1}{2}$ SP-1240DA on Supelcoport
PROGRAM: 80°C.-0 Minutes 8°/Minutes to 150°C
DETECTOR: Flame Ionization

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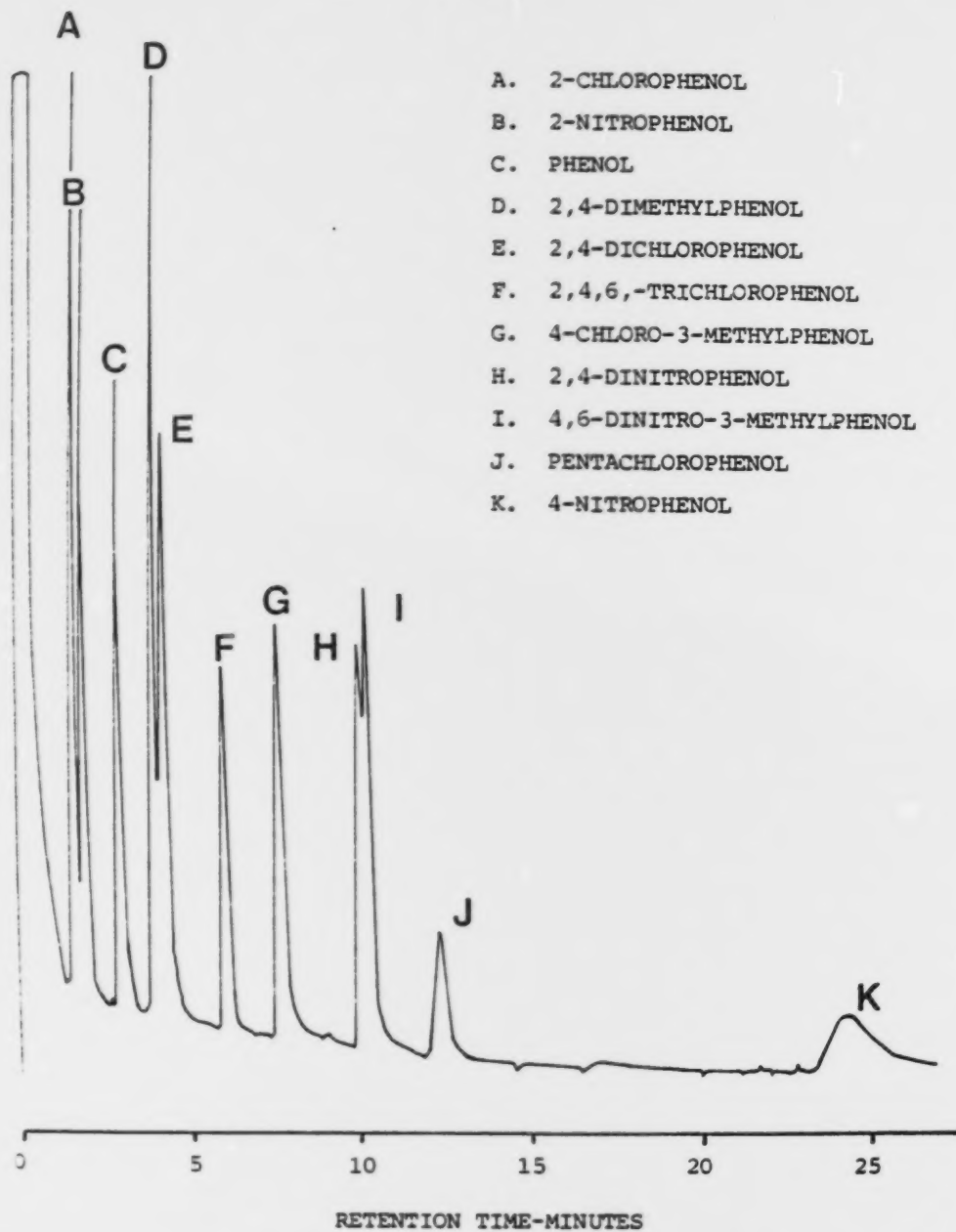


Figure 3. Gas Chromatogram of Phenols

TABLE 8. FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS

Compound	Retention Time
2-Chlorophenol	1.70
2-Nitrophenol	2.00
Phenol	3.01
2,4-Dimethylphenol	4.03
2,4-Dichlorophenol	4.30
2,4,6-Trichlorophenol	6.05
4-Chloro-3-methylphenol	7.50
2,4-Dinitrophenol	10.00
4,6-Dinitro-2-methylphenol	10.24
Pentachlorophenol	12.42
4-Nitrophenol	24.25

Column Conditions: Supelcoport 80/100 mesh coated with 1% SP-1240 DA in 6 ft long X 2 mm I.D. glass column with nitrogen carrier gas at 30 mL/min flow rate. Column temperature is 80°C at injection, programmed immediately at 8°C/min to 150°C final temperature.

Derivatization

The problems described in the Gas Chromatography section and the desire to be in compliance with IT Enviroscience's contractual commitment made it necessary to develop a derivatization technique to enhance the category compounds' EC sensitivity.

Preparation of β -chloroesters of the category phenols was attempted by using chloroacetic anhydride as the derivatizing agent by the following procedure. In a Teflon lined screw top vial, 0.1 g of chloroacetic anhydride, triple washed in petroleum ether, was added to 2 mL of a solution containing 1000 mg/L of each phenol in toluene. The vial was then heated to 80°C in a steam water bath for 30 minutes. The solution was then analyzed by GC/FID. Table 9 lists the columns evaluated for the separation of the β -chloroester derivatives of the phenols.

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TABLE 10. GC COLUMNS EVALUATED FOR CATEGORY 8 PFBB DERIVATIVES BY EC

GC Column No.	Packing	Description
1	OV-17	5% OV-17 on 80/100 mesh Chrom W-AW-DMCS; 1.8 m X 2.0 mm I.D. glass
2	OV-1	10% on 100/120 mesh Gas Chrom Q; 1.8 m X 2.0 mm I.D. glass
3	OV-225 + OV-1	1:1 blend of 3% OV-1 and 3% OV-225 on 80/100 mesh Gas Chrom Q; 1.8 m X 2.0 mm I.D. glass
4	SP-1240 DA	1% SP-1240 DA (R-1613) on 80/100 mesh Supelcoport; 1.8 m X 2.0 mm I.D. glass

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GC operating conditions are listed in Tables 11 and 12 for analysis of the pentafluorobenzyl phenol derivatives by GC/FID and GC/EC.

TABLE 11. GC CONDITIONS FOR CATEGORY 8
PFBB DERIVATIVES BY FID

FID temperature, °C	250
Injector temperature, °C	200
Oven temperature, °C	180
Carrier gas	Nitrogen
Carrier gas flow rate, cc/min	30

TABLE 12. GC CONDITIONS FOR CATEGORY 8
PFBB DERIVATIVES BY EC

EC detector temperature, °C	300
Injector temperature, °C	250
Oven temperature, °C	200
Carrier gas	95% argon/5% methane
Carrier gas flow rate, cc/min	30

GC columns 2 through 4 did not provide good separation of the derivatives. Column 1, 1.8 m long, 5% OV-17 on 80/100 mesh Chromosorb W-AW-DMCS, achieved excellent separation of all 11 derivatives and was selected as the column for use in future studies (Fig. 4).

GC/MS analysis indicated the absence of all the parent phenols and the presence of all the derivatives except the dinitrophenols. Conclusive identification of the dinitrophenols was not made, as the derivatives fragmented in the GC injection port. Identification of the fragment peaks as the pen-

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COLUMN: 5% OV-17 on Chromosorb W-AW

TEMPERATURE: 200°C

DETECTOR: Electron Capture

- A. PHENOL
- B. 2,4-DIMETHYLPHENOL
- C. 2-CHLOROPHENOL
- D. 4-CHLORO-3-METHYLPHENOL
- E. 2,4-DICHLOROPHENOL
- F. 2,4,6-TRICHLOROPHENOL
- G. 2-NITROPHENOL
- H. 4-NITROPHENOL
- I. PENTACHLOROPHENOL

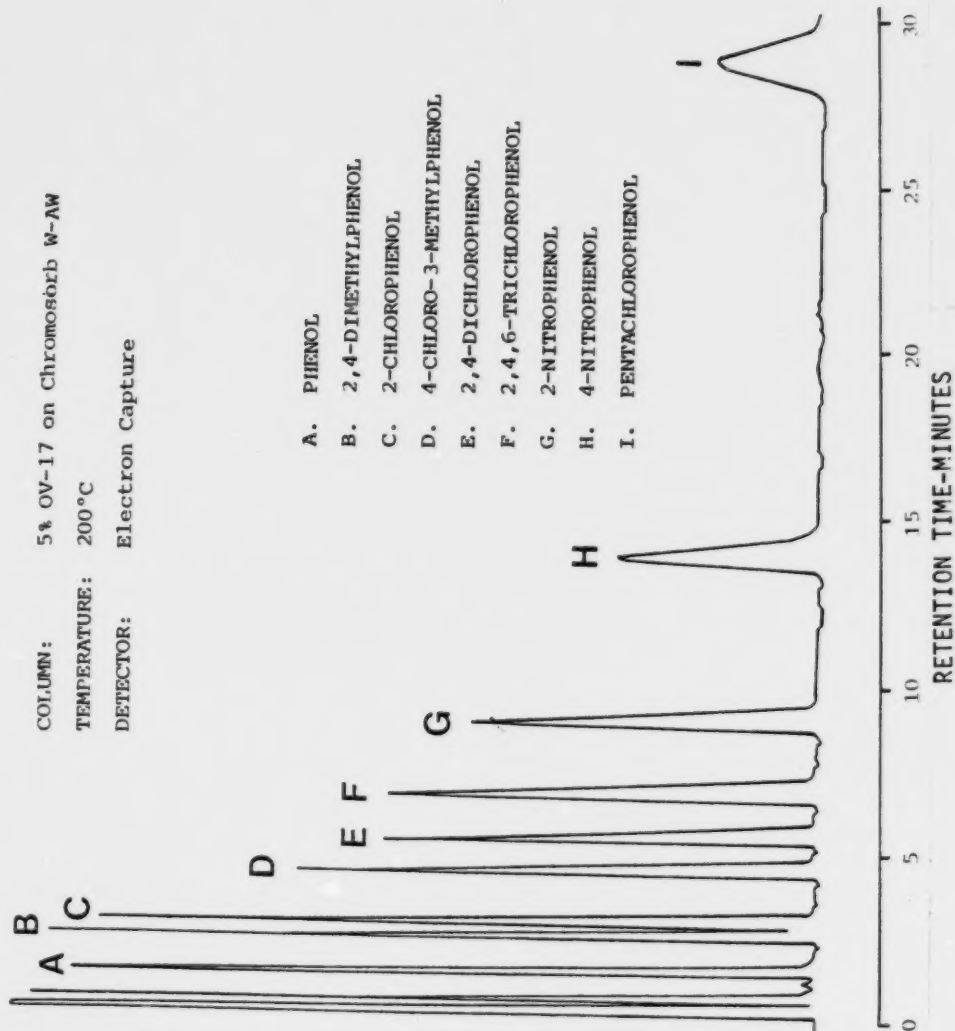


Figure 4. Gas Chromatogram of PFBB Derivatives of Phenols

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tafluorobenzyl ions and the dinitrophenol ions was considered to be adequate evidence of the presence of the dinitrophenols.

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The retention time, calculated minimum detection level, and practical minimum detection level of each derivative at 200°C on the OV-17 column are given in Table 13. The practical minimum detection level was defined at 10 mg/L in the concentrated extract or 10 µg/L in the water as a result of the linearity of the derivatives formed below this concentration being incomplete.

TABLE 13. RETENTION TIMES AND MDLs OF
CATEGORY 8's PFBB DERIVATIVES BY EC

Derivative	Retention Time (min)	Practical MDL (µg/L/H ₂ O)	Calculated MDL (µg/L/H ₂ O)
φOH	1.8	10	14.8
DMP	2.9	10	3.2
2-CP	3.3	10	7.4
4-Cl-3-MP	4.8	10	9.4
DCP	5.8	10	4.7
TCP	7.0	10	6.5
2-NP	9.1	10	6.4
4-NP	14.0	10	7.9
PCP	28.8	10	15
4,6-DN-2-MP	36.6	30 ^a	100
2,4-DNP	46.9	30 ^a	200

^aPractical MDL determined by GC/FID of underivatized compound since derivative formation at low concentrations was erratic.

When the solution containing the derivatized phenols was washed with distilled, deionized water, it yielded a much cleaner chromatogram. This procedure removed several interfering peaks, particularly those associated with the derivatizing agents.

Davis recommends that phenol solutions be taken to dryness below the derivatization step. This results in loss of the phenols to varying extents and the concentration of the derivative is lower than that of a sample that is theoretically equal in derivative concentration but has not been taken to dryness.

Derivatization of lower concentrations of the dinitrophenols, <100 mg/L, was found to be intermittently successful and quantitatively reliable to a level of 10 mg/L. A study was done to determine the optimum reaction time for the dinitrophenols. After reactions for two, four, and six hours at 80°C, four hours was found to be the optimum reaction time. Table 14 illustrates reaction time versus percent yield.

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TABLE 14. PERCENT YIELD OF DINITROPHENOL
PFBB DERIVATIVES VERSUS REACTION TIME

Reaction Time (hrs)	% Yield 2,4-DNP Deriv.	% Yield 4,6-DN-2-MP Deriv.
2	42.1	28.5
4	84.3	58.6
6	86.9	59.6

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Although the longer reaction time improved the derivatization procedure at the 100 mg/L level, concentrations in the 10 mg/L range did not give any significant yield (<5%) of the dinitrophenol derivatives. A larger, 60 fold mole-to-mole excess of derivatization agents was added without success. This excess, however, was successful when a higher concentration (2%) derivatization solution was used -- that is the same weight of derivatizing agents as before, but in a smaller volume of solvent. Samples with dinitrophenol concentration in the 10 mg/L range should be derivatized by adding a 60 fold mole-to-mole excess of a 2% derivatizing solution to total phenolic concentration.

However, to overcome analytical difficulties that hampered the analysis of dinitrophenols, their analyses were made by GC/FID rather than analysis of their PFBB derivatives by GC/EC. This overcame the poor analytical precision obtained with the derivative technique. The FID detection limits for all Category-8 compounds were given in Table 15. These detection limits were determined on the SP-1240 DA column run under the temperature program described in Table 8.

During this study it was observed that all the category phenols derivatized in 2-propanol as well as or better than in toluene. Sample clean up of the 2-propanol is accomplished by adding hexane after the derivatization reaction is complete. The sample can then be water washed, as is normally done.

The extraction of the PFBB derivatives from the reactant solution of 2-propanol was substituted with hexane because hexane, in comparison with toluene, demonstrated better extraction efficiencies without proportional increases in the amount of unknown impurities. Finally, upon completion of a short-term study of the derivatization of the phenols in 2-propanol solutions containing less than 10 mg/L, the data substantiated that the poor efficiency and precision data gathered at concentrations below 10 mg/L were the result of insufficient derivative recoveries. The final method indicates that the solvent extracts from 1 liter aqueous samples will be concentrated down to 10 mL of solvent substituted with 2-propanol and reduced to 1 mL with a two ball micro Synder column. The above concentration factor yielded higher and more reproducible results in aqueous solutions containing 10 µg/L.

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TABLE 15. FLAME IONIZATION DETECTION LIMITS - CATEGORY 8

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Compound	MDL (10 X Noise) ng Injected (1 μ l)	Water Concentration (μ g/L)
		MDL (10 X Noise) Water Concentration 1000 Fold
2-CP	2.0	2.0
2-NP	2.5	2.5
ϕ OH	1.4	1.4
DMP	1.7	1.7
DCP	2.1	2.1
TCP	5.0	5.0
4-Cl-3-MP	8.3	8.3
2,4-DNP	7.0	7.0
4,6-DN-2-MP	10.0	10.0
PCP	10.0	10.0
4-NP	10.0	10.0

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RESPONSE AND LINEARITY

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GC/FID response and linearity data on the four least EC-responsive phenols (2-chlorophenol, phenol, 2,4-dimethylphenol, and 4-chloro-3-methylphenol) and on the two dinitrophenols are presented in Table 16. All the compounds except the 2,4-dinitrophenol gave very linear response over the 10 to 1000 mg/L range. The 2,4-dinitrophenol was linear between 100 and 1000 mg/L; however, the response at 10 mg/L decreased dramatically. All GC/FID linearity data were generated under two isothermal conditions.

GC/EC response and linearity data on the seven most EC-responsive peaks in the $\mu\text{g/L}$ and low mg/L range are presented in Table 17. 2-Nitrophenol, 2,4-dichlorophenol, and 4-nitrophenol yielded straight linearity plots, with the lower concentrations giving a greater area response per unit concentration compared to that obtained with the higher concentrations. 2,4,6-Trichlorophenol was also linear; however, the highest concentration standard gave the greatest response per unit concentration. The response and linearity results for the dinitrophenols and pentachlorophenol were inconclusive, because tailing of the dinitrophenols prevented accurate quantification at the 0.1 mg/L to 2 mg/L levels. The tailing also obscured the 21 $\mu\text{g/L}$ pentachlorophenol peak and interfered with the 210 $\mu\text{g/L}$ peak, which prevented accurate linearity data from being obtained for that compound.

Response and linearity data on the pentafluorobenzyl derivatives over the 50 $\mu\text{g/L}$ to 50 mg/L range are presented in Table 18. In general the high concentration (<1 mg/L) standards have a greater area response per unit concentration than the low concentration standards. This may be due to adsorption of small amounts of derivative onto the GC column.

Pentafluorobenzyl Derivatives

The resolution between two peaks was calculated by the equation:

$$R = 2d/(W_1 + W_2) \quad (1)$$

The resolution of the two most adjacent pentafluorobenzyl derivative peaks, 2,4-dimethylphenol and 2-chlorophenol, was 0.95. A value of 1.0 indicated that the peaks were 98% resolved. Therefore they can be considered, for all practical purposes, to have been completely resolved.

Extraction Studies

Extractions from water were made of the 11 phenols by adding 50 mL of a concentrated buffer solution to 950 mL distilled, deionized water in a 2 liter separatory funnel. The concentrated buffer solutions used are listed in Table 19. The water samples containing the appropriate buffer were then pre-extracted with 100 mL hexane to minimize any impurities that may have been left.

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TABLE 16. RESPONSE AND LINEARITY OF SELECTED PHENOLICS ON FID

Compound	Concentration mg/L	Average Area mVsec
2-chlorophenol	12.4	19,187
	124	202,755
	1,240	1,927,857
phenol	9.4	24,652
	94	261,654
	940	2,453,785
2,4-Dimethylphenol	10	45,897
	100	476,926
	1,000	4,323,364
4-chloro-3-methylphenol	10	19,007
	100	220,851
	1,000	2,057,286
2,4-dinitrophenol*	15.6	3,971
	156.5	126,833
	1,565	1,860,373
4,6-dinitro-2-methylphenol*	16.3	18,520
	162.5	220,621
	1,625	2,347,386

Column: 4' 1% SP-1240 DA on 100/120 Supelcoport

Carrier gas: Nitrogen at 30 cc/min

Detector: FID at 250°C

Injector: 200°C

Column temperature: 100°C except where * indicates 150°C

Sample size: 2µL

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TABLE 17. RESPONSE AND LINEARITY OF SELECTED PHENOLICS ON EC

Compound	Concentration μg/L	Average Area mVsec
2-nitrophenol	98	3,314
	980	24,690
	9,840	172,965
2,4-dichlorophenol	105	7,679
	1,050	67,960
	10,460	527,321
2,4,6-trichlorophenol	9.9	5,791
	99	57,684
	990	699,164
2,4-dinitrophenol	1,600	Merged with below
	15,700	208,082
	156,500	9,126,132
4,6-dinitro-2-methylphenol	195	Merged with above
	1,950	736,091
	19,500	7,691,886
pentachlorophenol	21	-
	210	586,591
	2,060	1,537,662
4-nitrophenol	298	116,995
	2,980	905,368
	29,800	7,573,395

Column: 4' 1% SP-1240 DA
on 100/120 supelcoport

Sample size: 1 μL
Temperature: 150°C

Carrier gas: Argon/methane (5/95) at 30 cc/min

Detector: Electron capture at 300°C

Injector: 250°C

TABLE 18. RESPONSE AND LINEARITY OF PENTAFLUOROBENZYL BROMIDE DERIVATIVES ON EC

Compound	Concentration ($\mu\text{g/L}$)	Average Area (mVsec)	Compound	Concentration ($\mu\text{g/L}$)	(mVsec)
phenol	36.9	1,315	2-nitrophenol	50.2	1,593
	369	12,039		502	11,716
	3,690	196,501		5,020	182,575
	36,900	1,197,612		50,200	2,785,268
2,4-dimethylphenol	52.0	1,129	4-nitrophenol	39.6	1,969
	520	11,921		396	12,121
	5,200	206,860		3,960	149,783
	52,000	2,278,940		39,600	2,169,395
2-chlorophenol	37.8	705	pentachlorophenol	44.3	1,945
	378	7,670		443	10,745
	3,780	119,867		4,430	134,596
	37,800	1,607,074		44,300	1,863,880
4-chloro-3-methyl-phenol	57.6	1,547	4,5-dinitro-2-methylphenol	37.1	2,496
	576	12,297		371	11,091
	5,760	210,435		3,710	176,572
	57,600	2,699,535		37,100	3,280,400
2,4-dichlorophenol	39.8	1,015	2,4-dinitrophenol	22.2	11,257
	398	8,571		222	56,733
	3,980	131,024		2,220	956,966
	39,800	1,928,219		22,200	12,590,518
2,4,6-trichloro-phenol	43.9	1,421			
	439	11,005			
	4,390	151,366			
	43,900	1,838,775			

Column: 6' 5% OV-17 on 80/100 Chromosorb W-AW-DMCS

Column temperature: 200°C

Detector: Electron capture at 300°C

Injector: 200°C

Sample size: 1 μL
Temperature: 200°C

TABLE 19. SOLUTIONS NEEDED FOR
PREPARATION OF pH BUFFERS 2, 7, and 10

pH	Solutions*
2	74.6 g KCl + 0.212 l, 1.0 N HCl
7	13.6 g, KH_2PO_4 + 0.059 l, 1.0 NaOH
10	69.2 g NaHCO_3 + 0.35 l, 1.0 N NaOH

*Upon addition, dilute to 1 liter with distilled, deionized water.

A total of 24 samples were spiked with the phenols, eight at each pH level listed in Table 19. Each pre-extracted, buffered water sample was dosed with a cocktail containing the 11 phenols yielding an aqueous concentration of approximately 50 $\mu\text{g/L}$ of each compound (Table 20). Half the samples were extracted with dichloromethane and half were extracted with 15% diethylether/85% hexane (V/V).

Each extraction was performed by adding 60 mL of the appropriate solvent to the aqueous sample and extracting for two minutes. The solvent was then eluted through a Na_2SO_4 packed funnel (activated at 650°C) into a Kuderna-Danish receiver. The above procedure was repeated twice. The Na_2SO_4 funnel was then washed with two 10 to 20 mL portions of the solvent and drained into the Kuderna-Danish receiver which was fitted with a three ball Snyder column, and the solvent was evaporated to approximately 5 mL with steam heat. Ten mL of 2-propanol was then added to the Kuderna-Danish evaporator and the solvent reduced to a final volume of 2 milliliters. A 1 mL portion of this solvent was then derivatized to form the pentafluorobenzyl derivatives of the phenols and analyzed by GC/EC. Table 20 summarizes the extraction efficiencies and statistical analyses of the results.

The pH 2 dichloromethane extraction yielded the best overall efficiency, 75.6%, with the lowest level of impurities and was selected as the extraction technique for real world samples. At all pH levels high levels of interfering impurities were observed, precluding the quantification of many of the phenol derivatives. Generally, false positive results were obtained. At pH 7 the average extraction efficiencies for the phenols by dichloromethane were comparable to the efficiencies obtained at pH 2. However, the percent standard deviations for repetitive analyses were greater. While phenol, dimethylphenol, and 4-chloro-3-methylphenol were extracted with high efficiencies at pH 10, the remaining 8 phenols were not effectively extracted by dichloromethane at that pH.

Preservation Studies

Twenty-four 1 liter samples were prepared by adding 50 mL of the appropriate buffer to 950 mL of distilled, deionized water. The buffered water was pre-extracted with 100 mL hexane, the solvent decanted, and the water placed in clean, 1 liter bottles. Half the samples were spiked with 2 mL of a solution containing 66 mg/L of Cl_2 in water to yield samples with 1.2 mg/L of Cl_2 . All the samples were then spiked with a cocktail of the phenols so that the water samples had concentrations of approximately 50

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TABLE 20. EXTRACTION EFFICIENCIES AND PERCENT STANDARD DEVIATION OF
CATEGORY 8 (BASED ON EC ANALYSIS OF PFB DERIVATIVES)

pH	Solvent ^a Type	Buffer ^b Number	pOH	DMP	4-CL-				TCP	2-NP	4-NP	PCP	4,6-DN-	
					2-CP	3-MP	DCP	2-NP					2-MP	2,4-DNP
2	A	1	75.6 ^c 27.2 ^d	89.0 8.1	90.8 13.0	105.4 ^e 4.2	77.7 9.1	88.7 10.0	80.5 8.2	41.6 11.6	76.2 8.7	43.3 25.8	62.5 9.6	
2	B	1	f	71.4 12.2	f	f	89.3 ^h 19.1	97.9 ^h 28.7	87.8 ^h 18.3	102.6 ^h 49.3	103.6 ^h 21.7	g	f	
7	A	2	82.8 15.9	98.8 26.5	99.1 26.4	104.7 ^c 21.5	99.1 20.5	84.8 13.4	85.1 13.7	87.9 15.3	27.1 22.4	88.5 10.8	14.8 63.7	
7	B	2	f	129.3 73.4	f	f	f	106.3 4.1	f	f	f	67.7 30.9	g	
10	A	3	73.1 23.1	97.3 3.8	23.6 12.3	90.7 2.6	19.7 6.0	2.9 40.5	14.2 2.7	g	3.3 51.4	f	g	
10	B	3	85.3 51.5	70.8 10.3	26.4 42.9	20.1 19.3	21.5 6.7	5.8 9.4	5.8 63.6	5.4 87.3	7.9 25.7	44.6 99.8	28.9 75.1	
Concentration H ₂ O (µg/L)			49.9	50.5	49.7	50.8	47.4	53.6	48.9	49.0	45.0	49.8	51.1	

^aType A: Dichloromethane

^bBuffer No. 1: HCl/KCl

^cBuffer No. 2: KH₂PO₄/NaOH

^dBuffer No. 3: NaHCO₃/NaOH

^eCopper number percent recovery

^fLower number relative standard deviation

^gValue assumed to be 100% for future calculations

^hInterference prevented quantification

ⁱPeak not seen, derivative apparently not formed

^jPeak inaccurately quantified due to interference

ug/mL of each phenol. Half the samples were stored for seven days at 4°C, and half were stored for seven days at ambient temperature (23°C). All the samples were kept in the dark for the entire seven day period. The samples were then adjusted to pH 2 and extracted with the technique described in the extraction section. Table 21 summarizes the pH, temperature, Cl₂ concentration, and percent recovery after preservation for seven days. Each set of data represents the average of two identical samples stored under identical conditions.

Table 22 summarizes the percent loss due to preservation at the two most successful conditions. This was calculated by subtracting the average percent recovery for each compound from the dichloromethane extraction efficiency at a pH of two: the nonchlorinated pH 7 and pH 10 samples stored at 4°C had the lowest level of change in phenol concentrations and the fewest artifact peaks. Both increases and decreases in component concentrations were observed at both pH conditions. Table 22 summarizes the percent loss or gain in each component's concentration after a seven day storage period.

The pH 7 sample had a large increase in 2-chlorophenol and large decreases in 4-nitrophenol and the dinitrophenols. The remaining phenols had acceptable variation, with the largest loss occurring in the nonchlorinated, nonnitrated compounds phenol and 2,4-dimethylphenol.

The pH 10 samples demonstrated equivalent levels of loss of the phenol and 2,4-dimethylphenol. The only other significant variation was an increase over the expected level of recovery. The relative cleanliness of the chromatograms and the absence of new significant artifact peaks indicated that the higher levels of recovery were probably due to higher extraction efficiencies than was previously observed in the extraction studies. The reason for the increase in extraction efficiency is unknown, and further study will be necessary to ascertain which preservation technique is superior. With the higher levels of recovery assumed to be due to improved extraction efficiency and not to simultaneously eluting artifacts, the pH 10 preservation technique would be the method of choice. Under ambient and chlorinated storage conditions at the same pH, there were higher levels of interference and lower percents of recoveries, indicating that the 4°C and 0 mg/L Cl₂ conditions minimize compound loss and artifact formation. Water samples should be treated with 35 mg of sodium thiosulfate per mg/L of Cl₂ per liter of water immediately after collection to remove free chlorine from the sample.

Solvent Stability

Initially it was determined that the phenols would not derivatize to any appreciable extent in the presence of a ketone. The 2-butanone portion of the stability study was therefore abandoned and only 2-propanol was studied.

A standard containing approximately 100 mg/L of each of the 11 phenols was prepared, with 2-propanol used as the solvent and 3 mL of the solvent was added to each of 30 5-mL ampules. The ampules were cooled to 4°C to minimize the possibility of vapor ignition, then flame sealed, placed in

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TABLE 21. AVERAGE PERCENT RECOVERY OF PHENOLS FOLLOWING PRESERVATION FOR SEVEN DAYS
PFBB DERIVATIVES

pH	Cl ₂ Con. (µg/L)	Temp. (°C)	φOH	DMP	2-CP	4-C1- 3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN- 2-MP	2,4-DNP
2	0	Amb.	68.8	101.1	a	167.1	101.6	101.8	88.5	40.7	76.8	180.7	252.4
2	0	4	72.1	99.2	a	139.8	107.7	96.2	96.2	67.5	87.2	314.3	139.6
2	1.2	Amb.	31.1	273.6	340.9	50.9	76.6	144.6	102.2	78.0	97.0	163.5	54.1
2	1.2	4	30.8	98.7	323.8	40.4	78.9	162.4	102.1	73.7	106.2	100.0	38.4
7	0	Amb.	63.7	90.8	61.7	85.0	87.5	90.5	96.3	13.9	85.8	1.9	75.1
7	0	4	65.7	93.2	132.0	85.0	78.3	83.8	83.2	14.8	86.8	1.2	22.2
7	1.2	Amb.	12.9	140.8	143.8	24.3	0.7	51.6	9.0	100.4	31.9	b	b
7	1.2	4	22.8	179.6	151.5	16.9	1.6	60.4	13.0	221.3	75.3	b	b
10	0	Amb.	55.9	70.1	89.8	86.6	106.1	97.9	87.3	37.1	83.7	173.6	85.1
10	0	4	65.6	96.2	92.8	80.7	95.2	96.0	97.9	38.9	89.0	76.9	95.7
10	1.2	Amb.	41.0	289.9	71.6	181.7	41.2	608.3	72.4	317.2	304.5	54.5	88.9
10	1.2	4	32.3	143.8	37.5	89.7	22.7	559.9	84.4	137.9	259.1	53.0	44.2
H ₂ O concentration (µg/L)			49.9	50.5	49.7	50.8	47.4	53.6	48.9	49.0	45.0	49.8	51.1

GC/EC analysis performed on PFBB derivatives of extracts.

a Interference precluded quantification.

b Erratic generation and detection of derivatives precluded evaluation of preservation

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TABLE 22. AVERAGE PERCENT CHANGE OF PHENOLS FOLLOWING PRESERVATION WITHOUT CHLORINE AT TWO pHs

pH	Key	φOH	DMP	2-CP	4-Cl-3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN-3-MP	2,4-DNP
2	A	75.6	89.0	90.8	100.0	77.7	88.7	80.5	41.6	76.2	43.3	62.5
7	B	65.7	93.2	132.0	85.0	78.3	83.8	83.2	14.8	86.8	1.2	22.2
	C	-9.9	+4.2	+41.2	-15.0	+0.6	-4.9	+2.7	-26.8	+10.6	-42.1	-40.3
10	B	69.6	96.2	92.8	80.7	95.2	96.0	97.9	38.9	89.0	76.9	95.7
	C	-10.0	+7.2	+2.0	-19.3	17.5	+7.3	+17.4	-2.7	+2.8	+33.6	+33.2

GC/EC analysis performed on PFBB derivatives.

A = pH-2 Dichloromethane/extraction efficiency

B = Percent recovery after seven days

C = Percent loss due to preservation

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open test tube racks, and stored on a bench top under normal laboratory lighting conditions (fluorescent) for the duration of the study.

Three ampules of each were opened immediately after they were flame sealed and analyzed against the standard used to fill the ampules. On subsequent 30 day intervals for a total of 90 days, three ampules of each standard were opened and analyzed against a freshly prepared standard. Table 23 summarizes the stability of the Category-8 phenols in 2-propanol.

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Most anomalies presented in Table 23 were due to the evolution of the pentafluorobenzyl derivatization procedure during the 90 day period. A separate 90 day stability study for the dinitrophenols and 4-nitrophenol was conducted to explain the variability indicated in Table 23. The results of the study are given in Table 24.

TABLE 24. AVERAGE PERCENT CHANGE OF
NITRATED PHENOLS IN 2-PROPANOL AFTER DERIVATIZATION

Derivative	Day 0	Day 30	Day 60	Day 90
4-NP	-5.5	0.6	-9.6	-0.1
4,6-DN-2-MP	-5.8	+7.0	+0.2	-6.9
2,4-DNP	-6.3	-0.1	+2.9	-4.5

Clean Up Procedures

The experimental data gathered in this phase of the method development were obtained to illustrate that wastewater effluents containing Category 8 compounds could be efficiently screened and analyzed. Before the data were gathered, clean up procedures were perfected to eliminate interferences in the analyses. Then the accuracy and precision of the analytical methods for various industrial and municipal effluents were checked. This advance planning resulted in an economical, accurate method for the analytical study.

A review of the literature indicated that the clean up scheme for pesticides, in which Florisil was used as the adsorbent and petroleum ether was used as the eluant, should be an efficient method for phenols.(48) The experimental data accumulated from this method yielded recoveries ranging from 6 to 86% for the PFBB derivatives. The bulk recovery of the PFBB derivative occurred in the first fraction of 200 mL of petroleum ether. To increase recoveries, the eluant was changed to methanol. Recoveries did increase from 15 to 94%. The recovery data for the methanol fraction illustrated a definite increase, but the petroleum ether fraction cleaned up four unknown peaks that eluted near the compounds of interest. The methanol only cleaned up one of the four unknown peaks (Table 25).

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TABLE 23. AVERAGE PERCENT CHANGE OF CATEGORY 8 IN
2-PROPANOL AFTER DERIVATIZATION

Derivative	Concentration (mg/L)	Day 0	Day 30	Day 60	Day 90
ϕ OH	100	- 0.2	+ 2.4	+ 4.9	- 1.3
DMP	101	- 0.2	+ 3.3	-12.1	- 2.6
2-CP	99	-26.4	- 0.4	+26.1	+ 1.4
4-C1-3-MP	102	+ 2.5	- 3.6	- 8.6	+ 3.7
DCP	95	- 8.2	- 2.4	- 9.6	+ 2.7
TCP	107	- 1.7	+ 2.1	- 9.2	-14.2
2-NP	98	- 2.6	- 4.0	+16.2	-11.5
4-NP	98	- 2.6	-77.1	-48.8	-64.4
PCP	90	- 1.4	- 1.6	- 2.6	+ 4.1
4,6-DN-2-MP	100	-37.3	+15.5	-10.9	+11.5
2,4-DNP	102	-28.2	-13.5	-19.6	-26.4

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TABLE 25. AVERAGE PERCENT RECOVERY OF
PFBB DERIVATIVES AFTER FLORISIL COLUMN CLEAN UP

Derivative	Concentration (mg/L)	First Fraction (200 mL Petroleum Ether) Percent Recovery	First Fraction (200 mL Methanol) Percent Recovery
ϕ OH	11.0	86	89
2,4-DMP	9.5	83	91
2-CP	10.0	65	69
4-Cl-3-MP	10.2	78	62
DCP	9.2	77	45
TCP	10.1	80	69
2-NP	9.4	66	94
4-NP	15.0	38	70
PCP	9.7	70	71
4,6-DN-2-MP	10.0	42	92
2,4-DNP	9.9	6	15

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As a preliminary clean up step, the sample extraction procedure was altered by adjusting the pH to 12, extracting and re-adjusting the pH to 2, and then reextracting the sample. The pH 12 back extraction was incorporated to remove any base/neutral chlorinated compounds from the sample before determination of the chlorinated phenols. The recovery data after a pH 12 preliminary extraction of sample are given in Table 26.

TABLE 26. AVERAGE PERCENT RECOVERY OF CATEGORY 8
AFTER pH 12 BACK EXTRACTION (BASED ON FID ANALYSIS OF
UNDERIVATIZED PHENOLS)

Derivative	Water Concentration (mg/L)	Percent Recovery
2-CP	1.42	92
2-NP	1.01	94
ϕ OH	1.34	52
2,4-DMP	1.15	79
DCP	1.47	96
TCP	1.41	100
4-Cl-3-MP	1.00	100
2,4-DNP	2.67	74
4,6-DN-2-MP	2.44	103
PCP	1.96	91
4-NP	2.46	53

The use of an alternate clean up column of silica gel proved to be the superior vehicle for wastewater clean up of the PFBB derivatives. The

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complete methodology, including the previously mentioned pH 12 back extraction, was applied to a silica gel column with the following procedure and elution scheme. The preliminary silica gel column chromatography work was done by prewashing the column with hexane, loading the derivatized sample in toluene, and then desorbing with 5% toluene in hexane, 25% toluene in hexane, 50% toluene in hexane, and toluene. The present silica gel column chromatography scheme consisted of hexane pre-elution, loading the derivatized sample as a hexane solution, 20 mL hexane for the first fraction, and 20 mL toluene for the second fraction.

Although this method provided a relatively efficient means of clean up for the derivative, it failed to yield consistent data. Since the silica gel worked well on clean up, efforts were focused on finding a more satisfactory grade of silica gel to use for the clean up and column conditions that would be reproducible for accuracy and precision data.

After a short-term study, silica gel, grade 923, 100/200 mesh ACS, from Fisher Scientific Company was selected. Preparation consisted of activation at 130°C overnight, storage in a desiccator, and equilibration at room temperature before the silica gel was used. The column, 1 by 10 cm, was packed dry with 4 g of silica gel with a 2 g sodium sulfate cap. The column was pre-eluted with 6 mL hexane. Two mL of sample in hexane was loaded on the column and eluted with the following:

- Fraction 1: 10 mL of hexane
- Fraction 2: 10 mL of 15% toluene in hexane
- Fraction 3: 10 mL of 40% toluene in hexane
- Fraction 4: 10 mL of 75% toluene in hexane
- Fraction 5: 10 mL of 15% IPA in toluene

The composition of each fraction and the related percent of recovery are listed in Table 27 (Figs. 5 through 10). The eluates need not be concentrated again before they are analyzed by GC/EC.

Wastewater Application

All final extraction, clean up, and chromatographic procedures previously discussed were used for analyzing four Category-8 water samples:

- A. "Municipal Wastewater - Third Creek Station," obtained at Knoxville, TN
- B. "Final Effluent" received from Midwest Research Institute, Houston, TX on Dec. 14, 1978
- C. "Plastics Industry" received from R. Libby on April 5, 1978
- D. "Industrial Wastewater" received from D. Forest on Aug. 30, 1978

These samples were analyzed, as received, by GC/FID. The results of the analyses are listed in Table 28.

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TABLE 27. AVERAGE PERCENT RECOVERY OF PFBB
DERIVATIVES AFTER SILICA GEL CLEAN UP

Derivative	Concentration (mg/L)	Fraction				
		1	2	3	4	5
ϕ OH	110	-	-	90	10	-
DMP	95	-	-	95	7	-
2-CP	100	-	-	90	<1	-
4-Cl-3-MP	102	-	-	84	14	-
DCP	92	-	-	95	<1	-
TCP	101	-	50	50	-	-
2-NP	94	-	-	-	9	90
4-NP	150	-	-	-	<1	90
PCP	97	-	75	20	-	-

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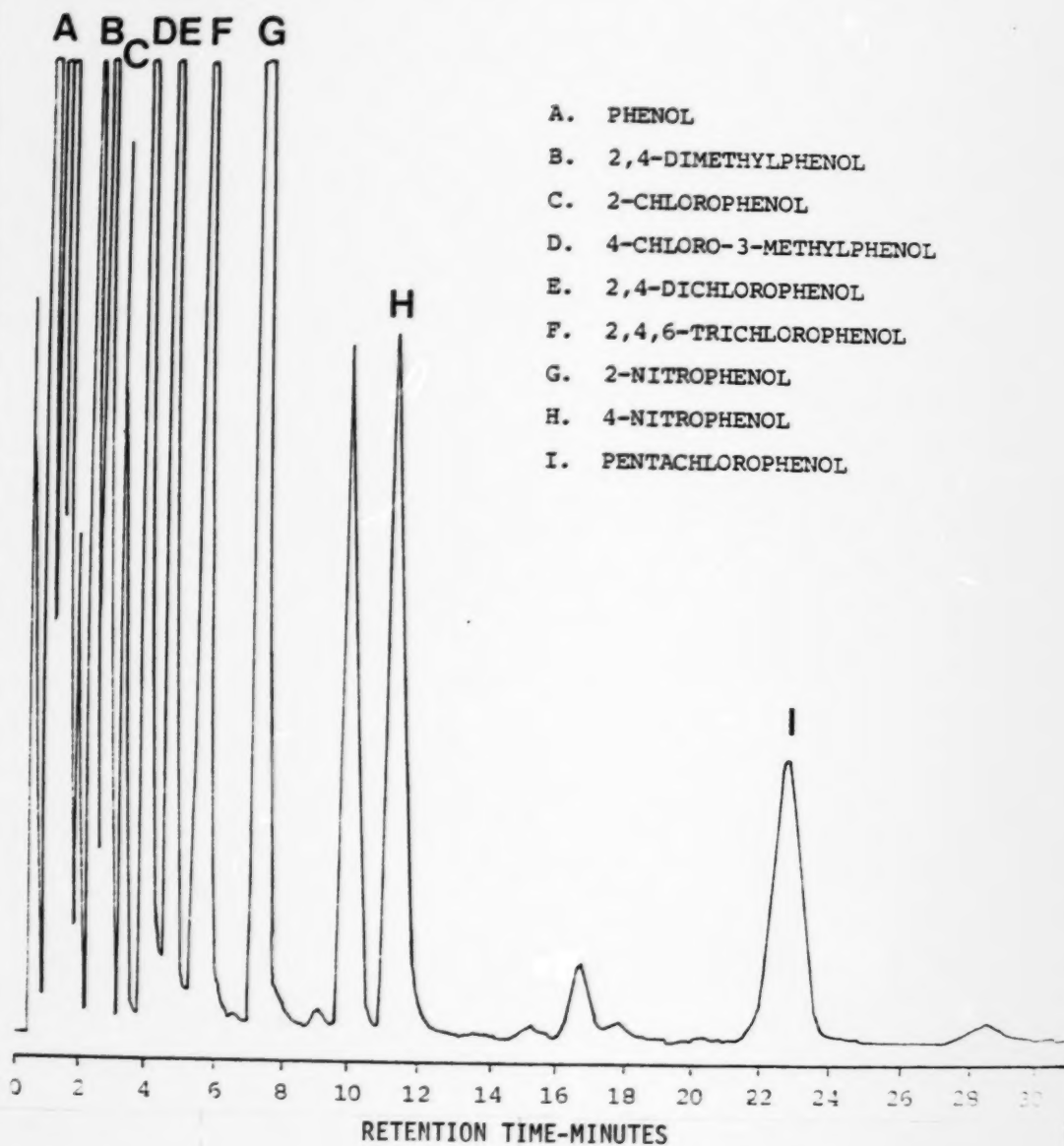


Figure 5. Analysis of Standard Solution Prior to Column Chromatography

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SILICA GEL CHROMATOGRAPHY

FRACTION 1

Hexane

PFB DERIVATIVES

- A. PHENOL
- B. 2,4-DIMETHYLPHENOL
- C. 2-CHLOROPHENOL
- D. 4-CHLORO-3-METHYLPHENOL
- E. 2,4-DICHLOROPHENOL
- F. 2,4,6-TRICHLOROPHENOL
- G. 2-NITROPHENOL
- H. 4-NITROPHENOL
- I. PENTACHLOROPHENOL

RETENTION TIME-MINUTES

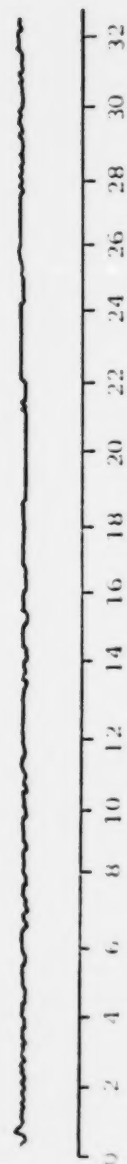


Figure 6. Fraction 1 - Column Clean up of Standard Solution

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SILICA GEL CHROMATOGRAPHY

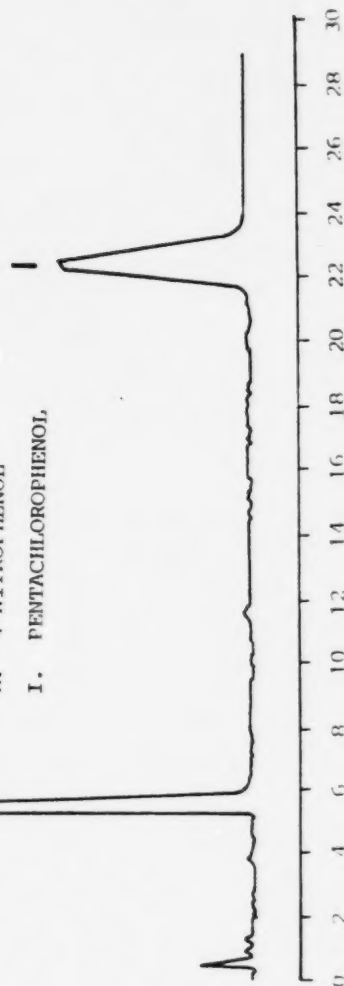
FRACTION 2

15% Toluene
in
Hexane

PFB DERIVATIVES

- A. PHENOL
- B. 2,4-DIMETHYLPHENOL
- C. 2-CHLOROPHENOL
- D. 4-CHLORO-3-METHYLPHENOL
- E. 2,4-DICHLOROPHENOL
- F. 2,4,6-TRICHLOROPHENOL
- G. 2-NITROPHENOL
- H. 4-NITROPHENOL
- I. PENTACHLOROPHENOL

F



RETENTION TIME-MINUTES

Figure 7. Fraction 2 - Column Clean up of Standard Solution

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SILICA GEL CHROMATOGRAPHY

FRACTION 3

50% Toluene
in
Hexane

PFB DERIVATIVES

- A. PHENOL
- B. 2,4-DIMETHYLPHENOL
- C. 2-CHLOROPHENOL
- D. 4-CHLORO-3-METHYLPHENOL
- E. 2,4-DICHLOROPHENOL
- F. 2,4,6-TRICHLOROPHENOL
- G. 2-NITROPHENOL
- H. 4-NITROPHENOL
- I. PENTACHLOROPHENOL

A B C D E

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0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30

RETENTION TIME-MINUTES

Figure 8. Fraction 3 - Column Clean up of Standard Solution

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SILICA GEL CHROMATOGRAPHY

FRACTION 4

75% Toluene
in
Hexane

PFB DERIVATIVES

- A. PHENOL
- B. 2,4-DIMETHYLPHENOL
- C. 2-CHLOROPHENOL
- D. 4-CHLORO-3-METHYLPHENOL
- E. 2,4-DICHLOROPHENOL
- F. 2,4,6-TRICHLOROPHENOL
- G. 2-NITROPHENOL
- H. 4-NITROPHENOL
- I. PENTACHLOROPHENOL

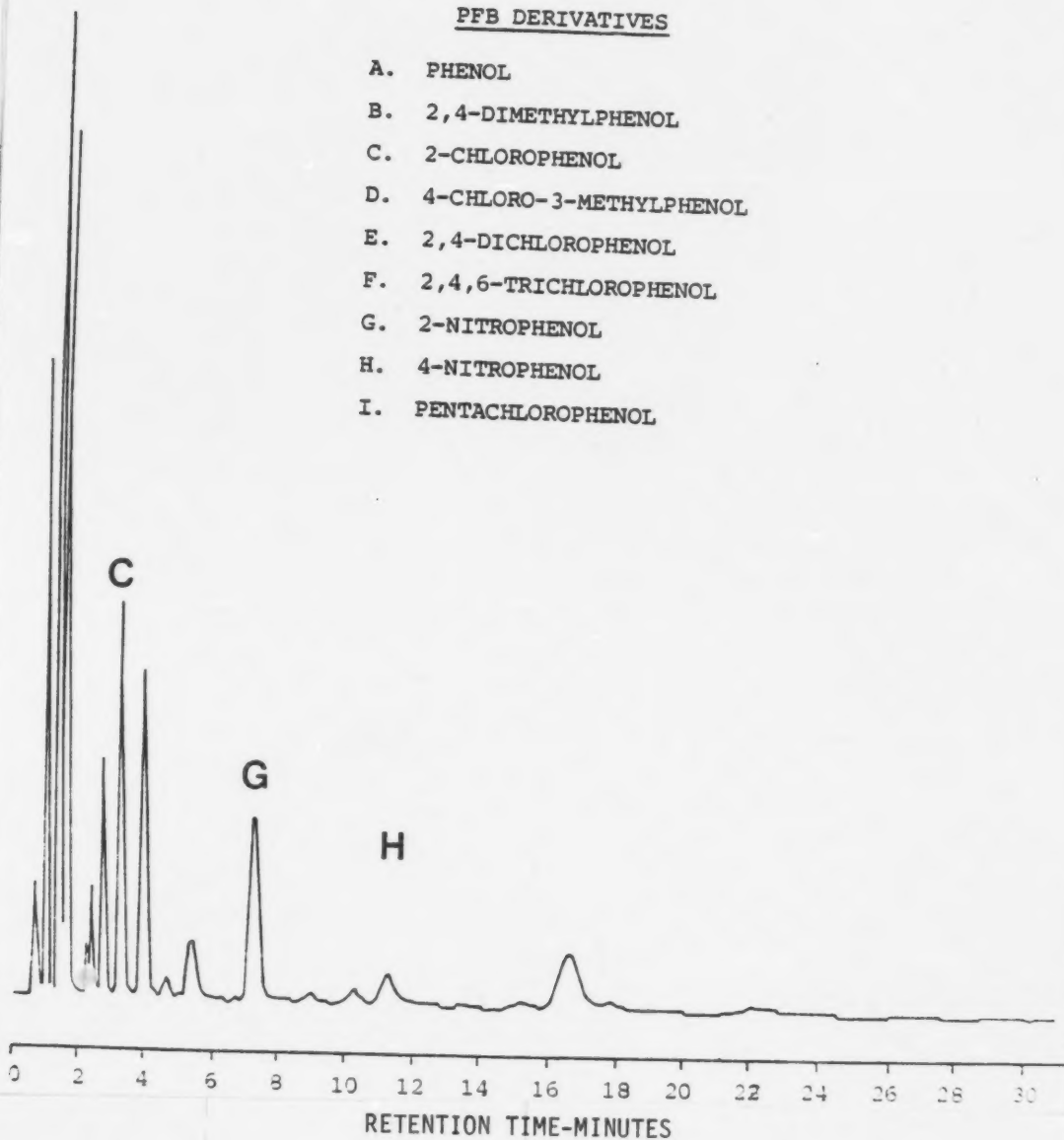


Figure 9. Fraction 4 - Column Clean up of Standard Solution

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SILICA GEL CHROMATOGRAPHY

FRACTION 5

15% IPA
in Toluene

PFB DERIVATIVES

- A. PHENOL
- B. 2,4-DIMETHYLPHENOL
- C. 2-CHLOROPHENOL
- D. 4-CHLORO-3-METHYLPHENOL
- E. 2,4-DICHLOROPHENOL
- F. 2,4,6-TRICHLOROPHENOL
- G. 2-NITROPHENOL
- H. 4-NITROPHENOL
- I. PENTACHLOROPHENAL

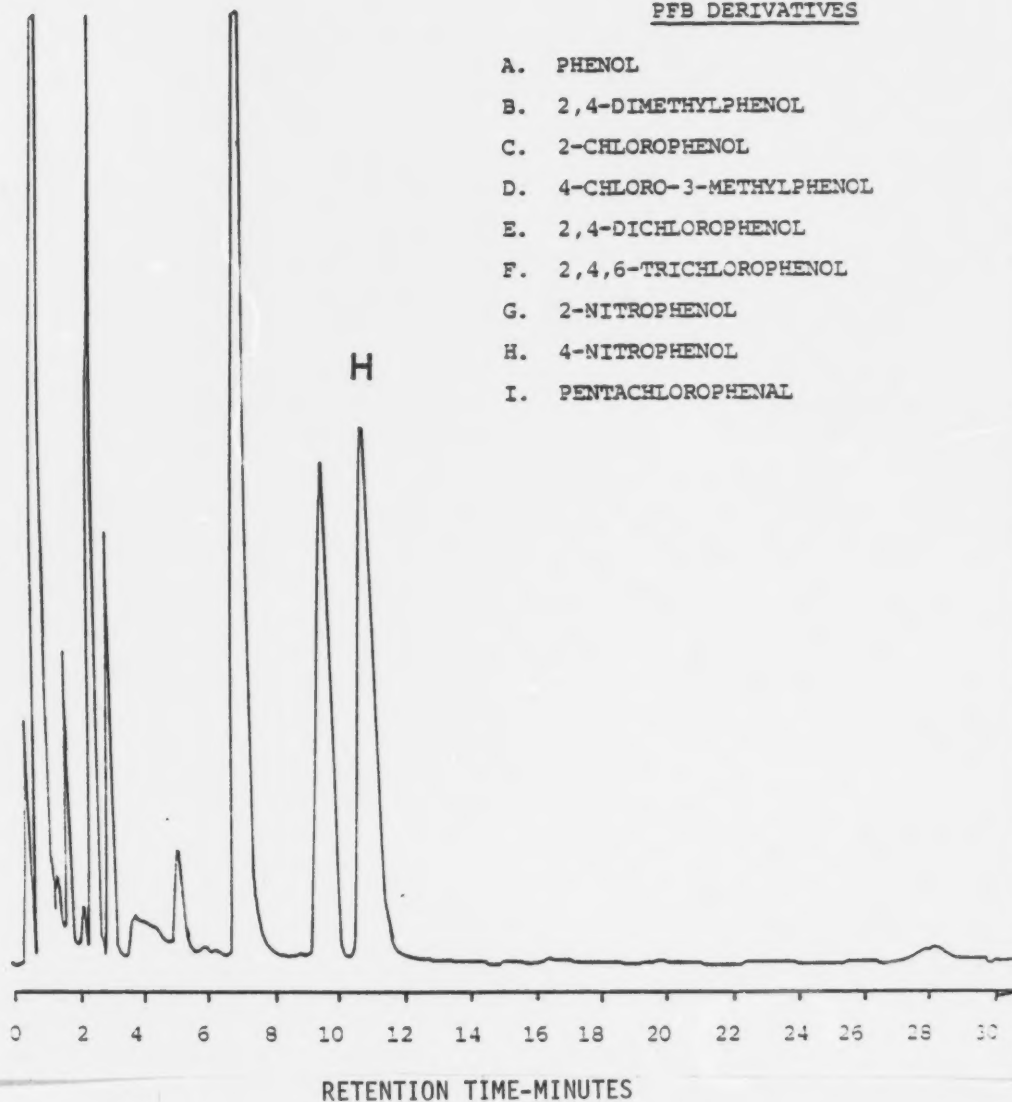


Figure 10. Fraction 5 - Column Clean up of Standard Solution

TABLE 28. WASTEWATER APPLICATION SAMPLE ANALYSIS^a
FID - UNDERIVATIZED PHENOLS

Sample ^b Number	φOH	DMP	2-CP	4-Cl- 3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN- 2-MP	2,4-DNP
A	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
B	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
C	190	<10	25	25	27	110	730	800	59	<10	<10
D	<10	<10	<10	<10	20	60	<10	<10	<10	<10	<10

^aConcentration expressed in µg/l.

^bA = "Municipal Wastewater - Knoxville Third Creek Station."

B = "Final Effluent Grab-12/14-78," received from Midwest Research Institute, Houston, Texas, on 12/14/78.

C = "Plastics Industry (15-05-CL-44 Final Effluent Grab)," received from R. Libby on 9/05/78.

D = "Industrial Wastewater: received from D. Foerst (EPA, Cincinnati, Ohio) on 8/30/78.

To better understand the method and sources of phenolic losses, wastewater A and a distilled water sample were spiked and analyzed by three methods:

1. FID without derivatization;
2. ECD after derivatization but without silica gel clean up;
3. ECD after derivatization and silica gel clean up.

From the above analyses, both the precision of the entire method and its accuracy were determined. The results are given in Tables 29 through 32.

A second wastewater received from the EPA on August 30, 1978, was spiked and analyzed by electron capture detection after derivatization and silica gel clean up. The results are given in Tables 33 and 34. Figures 11 through 15 are chromatograms of each column fraction.

TABLE 29. METHOD ACCURACY EXPRESSED AS PERCENT RECOVERY, BASED ON SPIKED, DISTILLED, DEIONIZED WATER

Method ^a	Sample	φOH	DMP	2-CP	4-Cl-3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN-2-MP	2,4-DNP
A	I	42	45	82	100	79	78	75	33	78	66	50
	II	41	28	85	91	89	92	84	36	90	97	54
	III	39	54	80	79	78	81	81	32	88	93	61
	$\bar{X}$	41	49	82	90	82	84	80	34	85	85	56
B	I	39	35	55	65	47	53	18 ^b	7 ^b	49	c	c
	II	62	35	64	63	66	67	79	31	79	c	c
	III	49	40	61	53	57	62	85	30	49	c	c
	$\bar{X}$	50	37	60	60	57	61	82	30	59	c	c
C	I	40	36	73	85	41	76	32	7	8	c	c
	II	61	36	80	82	58	93	163	41	97	c	c
	III	48	35	56	52	38	63	142	33	66	c	c
	$\bar{X}$	49	37	70	73	46	77	112	37	74	c	c
Concentration		88	126	142	98	146	108	112	118	126	150.4	190.8
(μg/L)												

^aA = Flame ionization detector analysis
 B = Electron capture without silica gel clean up
 C = Electron capture with silica gel clean up
^bRejected by critical T value test
^cDerivatives of the dinitrophenols were not formed

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TABLE 30. METHOD PRECISION EXPRESSED AS CONCENTRATION IN $\mu\text{g/L}$ BASED ON SPIKED, DISTILLED WATER^a
ELECTRON CAPTURE DETECTION OF DERIVATIVES FOLLOWING SILICA GEL CLEAN UP

Sample	Injection	ϕOH	DMP	2-CP	4-Cl-3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN-2MP ²	2,4-DNP ^c
I	1	35.1	55.0	129.4	104.9	75.3	109.0	32.7	7.9 ^b	93.3	87.53	100.8
	2	34.7	38.3	91.8	70.2	50.9	66.2	32.1	7.8 ^b	59.0	88.26	96.2
	3	34.8	41.3	89.2	75.7	54.3	70.2	42.6	10.8	67.8	104.00	98.1
II	1	54.2	55.6	138.2	99.6	107.8	123.9	186.9	55.1	149.4	156.31	96.2
	2	53.9	42.9	106.8	75.9	79.3	95.4	187.6	42.9	113.1	142.10	104.3
	3	52.1	37.5	93.8	65.6	68.8	83.6	173.0	47.6	102.2	139.25	106.3
III	1	45.0	47.4	85.4	53.4	57.9	70.6	146.4	37.5	82.2	132.22	118.4
	2	42.0	41.8	75.0	47.5	51.9	64.0	160.7	40.1	82.5	128.21	104.3
	3	39.0	44.3	79.1	51.0	55.5	68.6	170.2	37.8	84.8	159.19	121.1
True Value:		88.0	126.0	142.0	98.0	146.0	108.0	11.4	118.0	126.0	150.4	190.8
X		43.4	45.0	99.0	72.0	67.0	84.0	126.0	44.0	86.0	126.0	105.0
S		8.0	6.0	22.0	20.0	19.0	21.0	69.0	7.0	39.0	27.0	9.1

^aConcentration expressed in $\mu\text{g/L}$, without correction for recovery.

^bRejected by critical T value test.

^cDetermined by FID detection of underivatized compounds.

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TABLE 31. ACCURACY EXPRESSED AS PERCENT RECOVERY,^a
BASED ON A SPIKED, WASTEWATER SAMPLE (KNOXVILLE THIRD CREEK)

Method ^b Analysis	Sample Number	φOH	DMP	2-CP	4-Cl-3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN-2-MP	2,4-DNP
A	1	80	78	41	78	56	79	84	c	153	64	43
	2	53	58	97	93	46	60 ^d	61	c	136	41	50
	3	87	75	47	96	73	140	93	c	133	135	101
	$\bar{x}$	73	70	61	89	58	69	79		140	80	65
B	1	c	c	68	58	61	83	67	55	70	e	e
	2	c	c	53	47	43	72	57	40	33	e	e
	3	c	58	58	37	62	49	53	36	47	e	e
	$\bar{x}$		58	60	47	55	68	59	44	57	e	e
C	1	40	50	71	66	54	55	62	55	73	e	e
	2	31	54	68	88	65	78	61	64	53	e	e
	3	78	52	66	74	46	66	12	65	50	e	e
	$\bar{x}$	50	52	68	76	55	66	61	61	59	e	e
Concentration		88	126	142	98	146	108	112	118	126	150.4	190.8
		(μg/L)										

^apre-extracted at pH-12

^bA = Flame ionization detector analysis

B = Electron capture analysis without silica gel clean up

C = Electron capture analysis with silica gel clean up

^cImpurities cause too much interference for quantification

^dRejected by critical T value test

^eDerivatives were not generated

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TABLE 32. METHOD PRECISION EXPRESSED AS CONCENTRATION IN $\mu\text{g/L}$ ON A SPIKED WASTEWATER SAMPLE^a
ELECTRON CAPTURE DETECTION OF DERIVATIVES FOLLOWING SILICA GEL CLEAN UP

Sample Number	Injection	ϕOH	DMP	2-CP	4-C1- 3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN- 2-MP ^b	2,4-DNP ^b
I	1	34	58.7	97.9	64.9	62.8	59.0	77.7	31.6	70.5	95.6	82.1
	2	42	122.8 ^c	245.9 ^c	53.1	100.0	58.5	60.4	20.5	123.9	85.2	70.8
	3	30	67.2	105.1	76.0	72.6	61.0	70.2	25.8	83.1	106.1	92.1
II	1	26	130.8 ^c	256.8	116.6	126.7	68.1	74.2	76.8	19.9	60.9	94.9
	2	32	69.3	97.2	73.8	82.5	96.0	66.9	75.2	93.0	45.3	87.8
	3	24	66.7	92.9	70.5	74.5	89.6	62.2	23.7	85.4	74.4	102.0
III	1	63.9	74.7	109.3	75.0	77.7	82.9	18.8	106.2	76.9	202.9	193.4
	2	74.8	73.2	103.3	72.5	74.7	80.3	17.0	105.7	73.3	180.2	190.5
	3	67.0	49.4	70.2	46.7	48.0	51.6	5.4	101.5	39.5	220.8	182.5
True Value:		88.0	126	142	98	146	108	112	118	126	150.4	190.8
$\bar{X}$		44	65	96	72	80	95	68.6	93	74	119.1	121.8
S		19	9	13	19	22	29	7	16	17	64.9	51.1

^aWithout correction for recovery data; wastewater sample from Knoxville Third Creek.

^bDetermined by FID detection of underivatized compounds.

^cOutliers.

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TABLE 33. METHOD ACCURACY EXPRESSED AS PERCENT
RECOVERY BASED ON SPIKED, INDUSTRIAL WASTEWATER SAMPLE D

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Sample	ϕ OH	DMP	2-CP	4-C1- 3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN- 2-MP	2,4- DNP
1	53	59	122	58	132	93	a	a	73	a	a
2	39	29	65	27	64	46 ^b	a	a	84	a	a
3	42	39	90	40	113	97	a	a	135 ^b	a	a
$\bar{x}$	45	42	92	42	103	95			78		
C ^c	100	99.6	101	115	121	160	101	100	101	201	211
C ^d	100	99.6	101	115	101	100	101	100	101	201	211
C ₁	100	99.6	101	115	101	100	101	100	101	201	211
C ₂ ^e					20	60					

Sample received from D. Foerst, EPA, Cincinnati, Ohio, 8-30-78.

^aQuantification not possible due to interference from impurities.

^bRejected by critical T value test.

^cConcentration of the spiked sample in micrograms per liter.

^dConcentration of the spike added to the sample in micrograms per liter.

^eConcentration of the unspiked sample in micrograms per liter.

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TABLE 34. METHOD PRECISION EXPRESSED AS
CONCENTRATION IN $\mu\text{g/L}$ ON SPIKED, WASTEWATER SAMPLE D

Sample Number	ϕOH	DMP	2-CP	4-C1- 3-MP	DCP	TCP	2-NP	4-NP	PCP	4,6-DN- 2-MP	2,4- DNP
1	53	59	123	67	160	148	a	a	74	a	a
2	39	29	71	31	77	74 ^b	a	a	85	a	a
3	42	39	91	46	125	152	a	a	81	a	a
True value	100	100	101	115	121	160	101	100	101	201	211
$\bar{X}$	45	42	95	48	73	150			80		
S	7.4	15.3	26.2	18	54.6	2.8			5.6		

^aQuantification not possible due to interference from impurities.

^bRejected by critical T value test.

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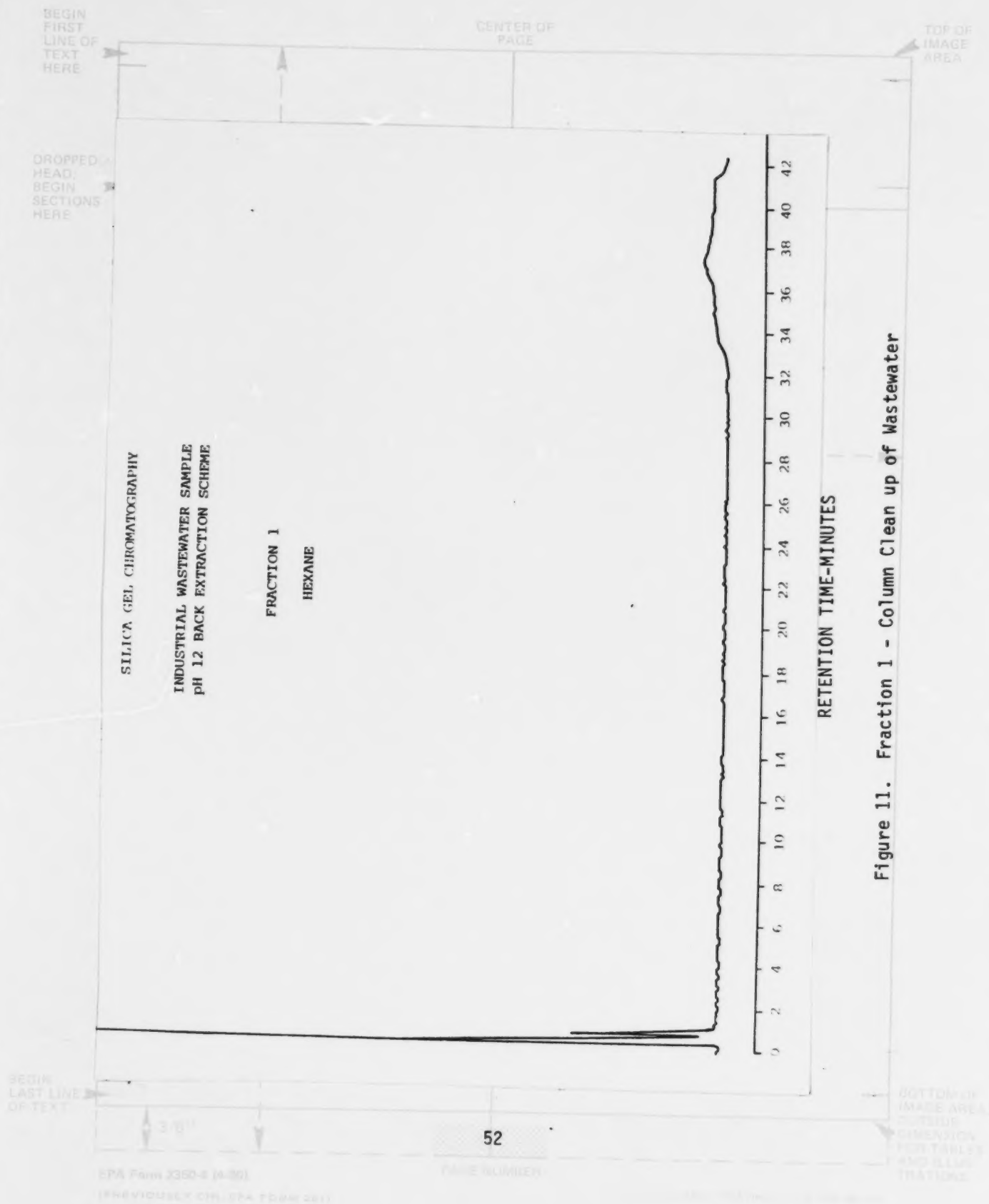


Figure 11. Fraction 1 - Column Clean up of Wastewater

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SILICA GEL CHROMATOGRAPHY

INDUSTRIAL WASTEWATER SAMPLE

pH 12 BACK EXTRACTION SCHEME

FRACTION 2

15% TOLUENE IN HEXANE

RETENTION TIME-MINUTES

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Figure 12. Fraction 2 - Column Clean up of Wastewater

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SILICA GEL CHROMATOGRAPHY

INDUSTRIAL WASTEWATER SAMPLE

pH 12 BACK EXTRACTION SCHEME

FRACTION 3

40% TOLUENE IN HEXANE

RETENTION TIME-MINUTES

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Figure 13. Fraction 3 - Column Clean up of Wastewater

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SILICA GEL CHROMATOGRAPHY

INDUSTRIAL WASTEWATER SAMPLE

pH 12 BACK EXTRACTION SCHEME

FRACTION 4

75% TOLUENE IN HEXANE

RETENTION TIME-MINUTES

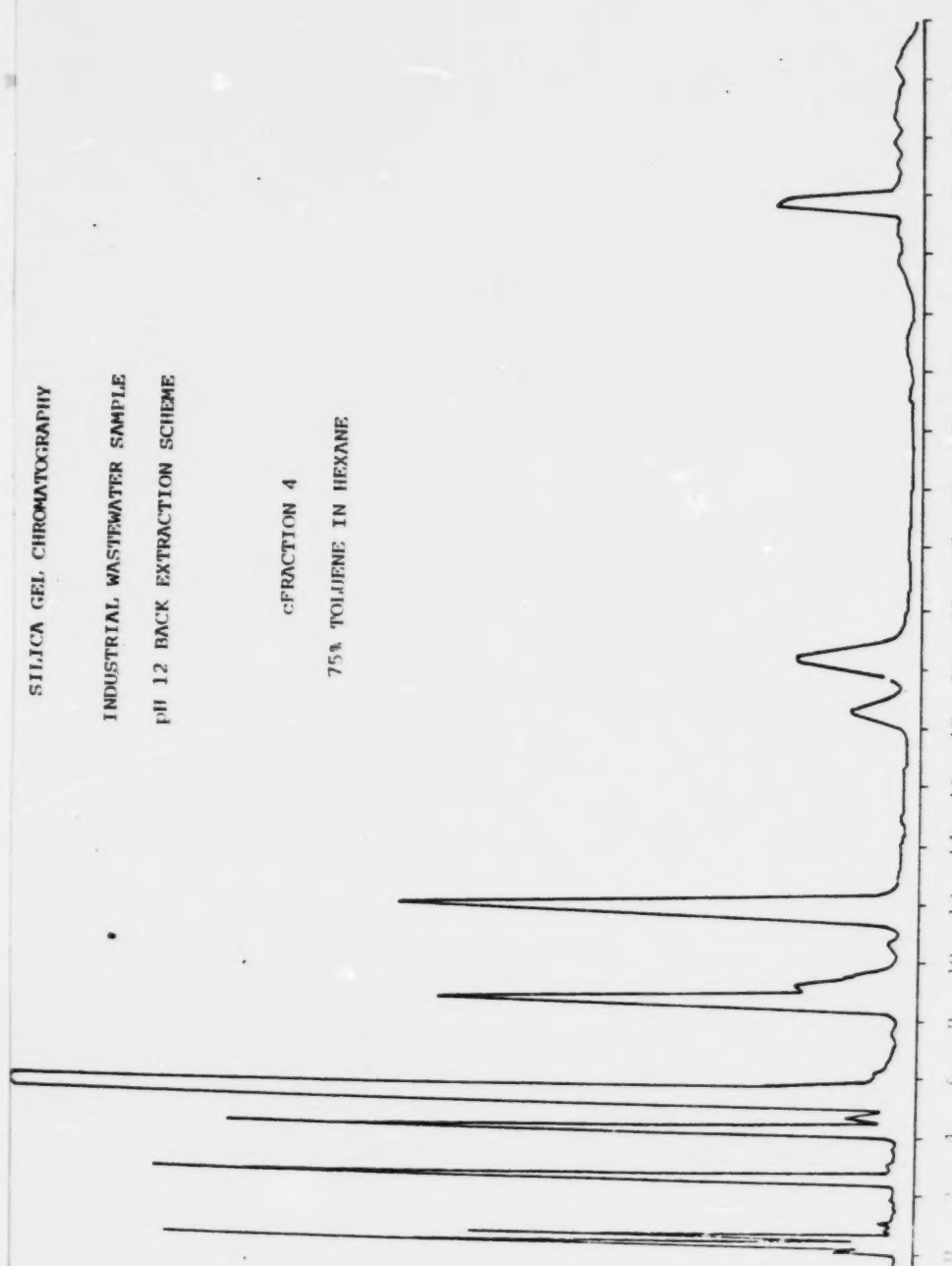


Figure 14. Fraction 4 - Column Clean up of Wastewater

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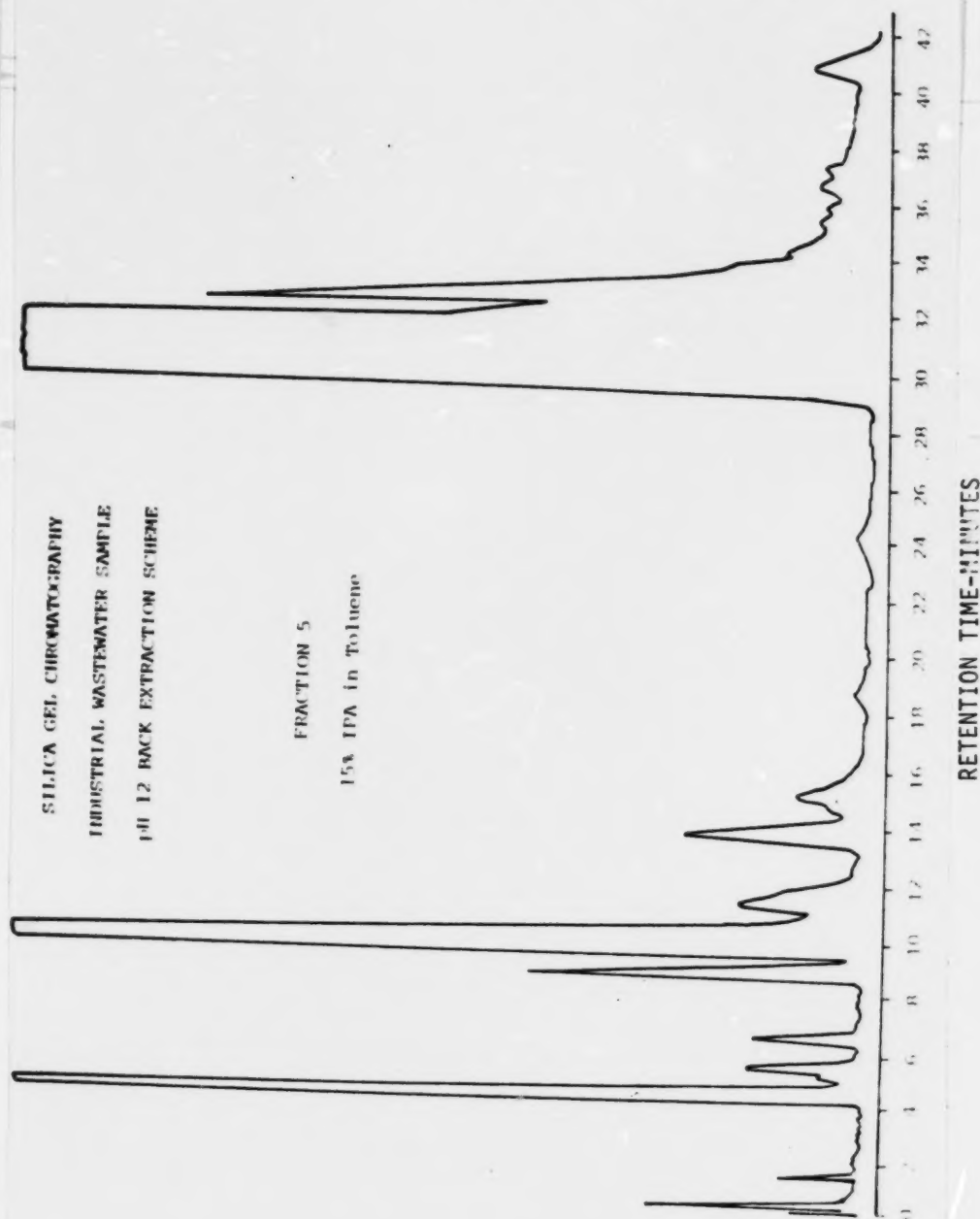


Figure 15. Fraction 5 - Column Clean up of Wastewater

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SECTION 5

SUPPLEMENTAL SEVEN DAY PRESERVATION STUDY - CATEGORY 8

INTRODUCTION

In the development and application of this test procedure, IT Enviroscience carried out preservation studies under different conditions for the subject compounds in clean distilled water only. The purpose of this brief study was to carry out a seven day preservation study of the subject compounds spiked into a real world wastewater following the preservation techniques outlined in the resultant EPA Method 604-Phenols (Appendix A).

EXPERIMENTAL

The wastewater selected for use in this study was a fresh sample of effluent wastewater from a Class B refinery which produces gasoline, kerosene, jet fuel, heating oil, heavy fuels and LPG. The wastewater treatment system consists of API oil/water separators, rapid sand filters, equalization tank, rotating biological contactors, and final clarifiers. Total flow from the plant is 3 to 4 MGD.

Using sulfuric acid, the pH of eight 1 liter bottles containing sample PBA was adjusted to 1 to 2 as measured by pH paper. Also, to each bottle was added 100 mg of sodium thiosulfate. Six of the eight samples were spiked with the subject compounds at concentrations ranging from 38 to 240 $\mu\text{g/L}$.

The bottles were mixed for 15 minutes and three of the spiked sample bottles and one unspiked sample blank were analyzed following EPA Method 604. The remaining bottles were refrigerated for seven days at 4°C and then analyzed by the same procedures. The results appear as Day 0 and Day 7 in Table 35.

DISCUSSION

The results presented in Table 35 represent the mean values from three spiked samples run on Day 0 and Day 7. The Day 0 recovery data were equal to or greater than the previous data presented in Section 4 of this report. The Day 7 data show a maximum loss after seven days of 50% for 4-nitrophenol and a minimum loss of 8% for 2,4-dinitrophenol. Overall, these losses are less than the previous data indicated.

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TABLE 35. SEVEN DAY PRESERVATION^a STUDY OF PHENOLS IN WASTEWATER

Compound	Spike Level ($\mu\text{g/L}$)	Mean Concentration ^b ($\mu\text{g/L}$)		Mean % Recovery ^b	
		Day 0	Day 7	Day 0	Day 7
2-CP	30.4	26.1	22.1	86	73
2-NP	150	134	83.6	73	56
ϕOH	91.2	38.8	30.4	43	33
DMP	37.6	31.4	19.4	84	52
DCP	129	119	82.0	92	64
TCP	59.0	58.4	43.1	99	73
4-Cl-3-MP	180	164	110	91	61
2,4-DNP	136	139	128	102	94
4,6-DN-2-MP	169	159	113	94	67
PCP	121	98.4	81.1	81	67
4-NP	240	131	65	55	27

^a Preservation technique outlined in EPA Method 604.

^b Results based on triplicate sample analysis.

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SECTION 6

INVESTIGATION OF THE MODIFIED FRITZ-CHRISWELL AND EMSL METHOD 604 FOR THE ANALYSIS OF CATEGORY 8 - PHENOLS

INTRODUCTION

This investigation was designed to evaluate the use of the Fritz-Chriswell method (46) as modified in the RETA methods. In order to accomplish this, comparison with results from the liquid-liquid extraction procedure method currently used by IT Enviroscience was done. This liquid-liquid extraction procedure was developed for EMSL and is included in the Interim Methods for Organic Compounds in Municipal and Industrial Wastewater as Method 604.

In this experiment the Modified Fritz-Chriswell A-26 method was compared to the Category-8 method by studying the respective results from analyzing both spiked and unspiked distilled water along with two spiked and unspiked wastewaters. The recovery of phenols from spiked samples and comparison of chromatograms for interferences were the basic parameters studied. The two wastewaters used in this study are described below:

Wastewater No. 1 - Effluent from an industrial wastewater treatment plant consisting of API oil/water separators, rapid sand filtering, equalization tank, rotating biological contacters, and final clarifiers. The wastewater source is a Class B refinery producing gasoline, kerosene, jet fuel, heating oils, heavy fuels, and LPG.

Wastewater No. 2 - Effluent from an industrial primary and secondary activated sludge treatment system followed by tertiary activated carbon treatment. Wastewater source is a large producer of inorganic and organic chemicals, including chemical intermediates and chlorinated and nitrated pesticides.

EXPERIMENTAL

Three samples composed of two wastewaters and one distilled water were analyzed in duplicate by each method before and after spiking. The results of their preliminary analyses are listed in Table 36. The samples were spiked with all eleven priority pollutant phenols at concentrations ranging from 110 to 370 micrograms per liter. After preparation of the above samples, they were:

1. Carried through the modified Fritz-Chriswell procedure, concentrated, pentane exchanged, and analyzed.

TABLE 36. PHENOL ANALYSIS BY BOTH MODIFIED FRITZ-CHRISWELL AND EMSL METHOD 604 (FID)

Compound	Distilled Water		Wastewater No. 1		Wastewater No. 2	
	F-C	L-L	F-C	L-L	F-C	L-L
2-CP	<10	<10	<10	<10	<10	14
2-NP	<10	<10	<10	<10	<10	<10
4-OH	<10	<10	<10	<10	<10	<10
2,4-DMP	<10	<10	<10	<10	<10	16
DCP	<10	<10	<10	<10	<10	<10
TCP	<10	<10	<10	<10	11	<10
4-C1-3-MP	<10	<10	<10	<10	20	48
2,4-DNP	<10	<10	12	<10	40	55
4,6-DN-2-MP	<10	<10	18	38	34	343
PCP	<10	<10	<10	68	<10	<10
4-NP	<10	<10	<10	<10	<10	<10

F-C Concentration in $\mu\text{g/L}$ determined by modified Fritz-Chriswell method.

L-L Concentration in $\mu\text{g/L}$ determined by EMSL Method 604 (FID).

2. Pre-extracted at pH 12 with dichloromethane, followed by extraction at pH 2 with dichloromethane, concentrated, exchanged to 2-propanol, and analyzed.

All samples were concentrated by a factor of 500, utilizing Kuderna-Danish apparatus.

The A-26 resin was purchased from Mallinckrodt and cleaned up by the procedure listed in the Modified Fritz-Chriswell A-26 Resin Method (Appendix B).

The analysis was performed by gas chromatography with flame ionization detection (FID). A Perkin-Elmer Sigma 3 was used with a 6' X 2 mm ID glass column, containing 1% SP-1240 DA on 80/100 mesh Supelcoport. The column temperature was 100°C at injection, programmed immediately at 8°C/min to 190°C. The injection size was 2 μ L. The data system was a Hewlett-Packard model 3380S recording integrator.

COMPARISON OF PERCENT RECOVERY

The information displayed in Table 37 indicates the recovery of phenols from spiked distilled water averaged 87.6% $\pm$ 4.6 using the Category-8 FID procedure and only 46.3% $\pm$ 12 when using the modified Fritz-Chriswell method with solvent exchange from acetone to pentane. The average recovery (Table 38) of phenols from spiked wastewater No. 1 was 84.6% $\pm$ 5.0 by the Category-8 method and only 39.4% $\pm$ 9.6 by the modified Fritz-Chriswell method with solvent exchange. The average recovery (Table 39) of phenols from spiked wastewater No. 2 was 87.6% $\pm$ 11 using the Category-8 method and 57.9% $\pm$ 21 by the same Fritz-Chriswell method.

COMPARISON OF CHROMATOGRAPHIC INTERFERENCES

Despite the elaborate clean up of the A-26 resin, the distilled water system blank analyzed by the Fritz-Chriswell method yielded a large unknown peak that eluted between TCP and 4-CL-3-MP on the 1% SP-1240 DA column. However, in neither case were there any interference peaks that eluted at the same retention time as the phenols of interest when analyzing the distilled water system blanks.

The presence of 4-C-3-MP, 4,6-DN-2-MP and PCP at concentrations of greater than 10 μ g/L in wastewater No. 1 was determined by Category-8 method analysis while only 2,4-DNP and 4,6-DN-2-MP were determined to be present at that concentration level by the Fritz-Chriswell method.

It is likely that the 2,4-DNP determined in wastewater No. 1 using the Fritz-Chriswell method is actually an interference peak due to the fact that the Category-8 method yielded much higher average recoveries for 2,4-DNP than the Fritz-Chriswell method in this study.

The presence of 2-CP, ϕ OH, 2,4-DCP, 2,4-DNP, and PCP at concentrations of greater than 10 μ g/L in wastewater No. 2 was determined by Category-8

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TABLE 37. COMPARISON OF ACCURACY BY TWO METHODS EXPRESSED AS
PERCENT RECOVERY OF PHENOLS FROM SPIKED DISTILLED WATER

Method	Sample	2-CP	2-NP	ϕ OH	DMP	DCP	TCP	4-Cl- 3-MP	DNP	4,6-DN- 2-MP	PCP	4-NP
Category 8 (FID)	1%R	89	91	48	87	95	94	91	92	90	96	50
	2%R	96	89	51	92	103	102	100	99	96	105	53
	A	185	312	252	122	186	200	374	320	298	226	280
	$\bar{X}$	93	95	50	90	99	98	96	96	93	101	52
	S	4.9	4.9	2.1	3.5	5.7	5.7	6.4	4.9	4.2	6.4	2.1
Fritz- Chriswell (FID)	1%R	30	33	26	<10	37	36	46	49	58	65	66
	2%R	58	59	23	17	62	70	63	42	52	70	40
	A	185	312	252	122	186	200	374	320	298	226	280
	$\bar{X}$	44	46	25	14	50	53	55	46	55	68	53
	S	20	18	4.9	4.9	18	24	12	4.9	4.2	3.5	18

R = Recovery

A = Spike concentration in $\mu\text{g/L}$

$\bar{X}$ = Mean percent recovery

S = Standard deviation from mean percent recovery

TABLE 38. COMPARISON OF ACCURACY BY TWO METHODS EXPRESSED AS
PERCENT RECOVERY OF PHENOLS FROM SPIKED WASTEWATER No. 1

Method	Sample	2-CP	2-NP	ϕ OH	DMP	DCP	TCP	4-C1- 3-MP	DNP	4,6-DN- 2-MP	PCP	4-NP
Category 8 (FID)	1%R	95	101	59	77	99	103	103	103	85	81	65
	2%R	85	91	54	71	89	93	93	103	85	78	52
	$\bar{X}$	90	96	57	74	94	98	98	103	85	80	59
	S	7.1	7.1	3.5	4.2	7.1	7.1	7.1	0.0	0.0	2.1	9.2
Fritz- Chriswell (FID)	A	<10	<10	<10	<10	<10	<10	38	<10	19	68	<10
	B	247	416	336	162	248	267	499	427	397	301	373
	C	247	416	336	162	248	267	537	427	416	369	373
	1%R	51	45	16	12	62	65	52	51	33	53	56
	2%R	24	40	8	8	43	40	29	40	41	48	41
	$\bar{X}$	38	43	12	10	53	53	41	46	37	51	49
	S	19	3.5	5.7	2.8	13	18	16	7.8	5.7	3.5	11
	A	<10	<10	<10	<10	<10	<10	<10	12	18	<10	<10
	B	247	416	336	162	248	267	499	427	397	301	373
	C	247	416	336	162	248	267	499	439	415	301	373

%R = Percent recovery
 $\bar{X}$ = Mean percent recovery
 S = Standard deviation of mean percent recovery
 A = Concentration (μ g/L) of the unspiked sample
 B = Spike concentration (μ g/L)
 C = Concentration of the sample including spike (μ g/L)

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TABLE 39. COMPARISON OF ACCURACY BY TWO METHODS EXPRESSED AS
PERCENT RECOVERY OF PHENOLS FROM SPIKED WASTEWATER NO. 2

Method	Sample	2-CP	2-NP	ϕ OH	DMP	DCP	TCP	4-C1- 3-MP	DNP	4,6-DN- 2-MP	PCP	4-NP
Category 8 (FID)	1%R	102	100	57	87	103	114	106	128	129	142	59
	2%R	80	84	40	78	86	102	93	115	117	100	48
	$\bar{X}$	91	92	49	83	95	108	100	122	123	121	54
	S	16	11	12	6.4	12	8.5	9.2	9.2	8.5	30	8.8
	A	14	<10	<10	<10	16	<10	<10	48	55	343	<10
Fritz- Chriswell (FID)	B	185	312	252	122	186	200	374	320	298	226	280
	C	199	312	262	122	202	200	374	368	353	569	280
	1%R	57	60	12	8	67	68	66	66	54	30	36
	2%R	27	53	<4	20	64	93	73	128	NQ	144	NQ
	$\bar{X}$	42	57	8.0	14	66	81	69.5	97	-	87	-
	S	21	4.9	5.7	8.5	2.1	18	4.9	44	-	81	-
	A	<10	<10	<10	<10	<10	<10	11	20	40	34	<10
	B	185	312	252	122	186	200	374	320	298	226	280
	C	185	312	252	122	186	200	385	340	338	260	280

%R = Percent recovery

$\bar{X}$ = Mean percent recovery

S = Standard deviation of mean percent recovery

A = Concentration (μ g/L) of the unspiked sample

B = Spike concentration (μ g/L)

C = Concentration of the sample including spike (μ g/L)

NQ = Not quantitated due to interferences

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method analysis while only 4-C-3-MP, 2,4-DNP, 4,6-DN-2-MP, and PCP were determined to be present at that concentration level by the Fritz-Christwell method. The absence of 2-CP, ϕ OH, and 2,4-DCP at 10 μ g/L using the Fritz-Christwell method is most likely due to the concentration levels of 2-CP, ϕ OH, and 2,4-DCP determined using the Category-8 method were between 10 and 16 μ g/L; therefore, their absence using the Fritz-Christwell method is best explained by the fact that the Fritz-Christwell method yields average recoveries of only one-half those of the Category-8 method for these three compounds.

Based on this investigation, neither method generated definite false positive results.

ANALYTICAL PROBLEMS ENCOUNTERED

IT Envirosience's experience with the Fritz-Chriswell method in the past has not involved solvent exchange from acetone to pentane. In this study two phases were discovered in the 10 ml Kuderna-Danish thimble after exchanging for pentane. The Fritz-Chriswell method (see Appendix B) contains no drying step. Since it is miscible with acetone, water will be carried through the procedure. In the worst case, the pentane layer was injected into the GC and again after making the small water layer extremely acidic, but no increase in recoveries was observed.

Because of the low recoveries experienced after pentane exchange, a limited study was designed in order to analyze both a spiked distilled water and a spiked wastewater No. 2 sample in acetone and after pentane exchange.

LIMITED FRITZ-CHRISWELL A-26 RESIN EXPERIMENT

The limited Fritz-Chriswell experiment consisted of analyzing the acetone eluates from both spiked wastewater No. 2 and spiked distilled water by GC/FID and duplicate samples analyzed using solvent exchange of the acetone eluate to pentane.

The analysis of spiked distilled water without solvent exchange resulted in average recoveries that were 21% greater than with solvent exchange. The average recoveries from spiked wastewater No. 2 were 33.4% greater without solvent exchange than with solvent exchange. The results from this limited study are presented in Tables 40 and 41.

CONCLUSIONS

Results of this investigation indicate that the Category-8 method is superior to the Modified Fritz-Chriswell A-26 method in average percent recovery. Based upon only duplicate analyses, the Category-8 procedure also displayed better precision. Results from the analyses of two unspiked wastewater samples by each method were inconclusive as to whether any false positive results were generated by either method.

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TABLE 40. PERCENT RECOVERY OF PHENOLS FROM SPIKED DISTILLED WATER WITH
AND WITHOUT SOLVENT EXCHANGE USING MODIFIED FRITZ-CHRISWELL METHOD

Compound	A	B	C	D	Percent Recovery with Acetone Solvent	Percent Recovery with Pentane Solvent
2-CP	<10	185	133	107	72	58
2-NP	<10	312	225	184	72	59
φOH	<10	252	101	83	40	33
2,4-DMP	<10	122	27	21	22	17
DCP	<10	186	140	115	75	62
TCP	<10	200	162	140	81	70
4-C1-3-MP	<10	374	295	233	79	62
2,4-DNP	<10	320	230	134	72	42
4,6-DN-2-MP	<10	298	203	155	68	52
PCP	<10	226	195	158	86	70
4-NP	<10	280	218	112	78	40

A - Concentration of the unspiked sample (pentane solvent) in µg/L.

B - Concentration of the spike added to the sample in µg/L.

C - Concentration of the spiked sample (acetone solvent) in µg/L.

D - Concentration of the spiked sample (pentane solvent) in µg/L.

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TABLE 41. PERCENT RECOVERY OF PHENOLS FROM SPIKED WASTEWATER SAMPLE NO. 2 WITH
AND WITHOUT SOLVENT EXCHANGE USING MODIFIED FRITZ-CHRISWELL METHOD

Compound	A	B	C	D	Percent Recovery with Acetone Solvent	Percent Recovery with Pentane Solvent
2-CP	<10	185	175	105	95	57
2-NP	<10	312	306	187	98	60
OH	<10	252	50	50	20	20
2,4-DMP	<10	122	17	10	14	8
DCP	<10	186	202	125	109	67
TCP	<10	200	218	136	109	68
4-C1-3-MP	11	374	378	247	98	63
2,4-DNP	20	320	282	211	82	60
4,6-DN-2-MP	40	298	289	161	84	41
PCP	34	226	395	68	160	15
4-NP	<10	280	294	101	76	8

A - Concentration of the unspiked sample (pentane solvent) in $\mu\text{g/L}$.

B - Concentration of the spike added to the sample in $\mu\text{g/L}$.

C - Concentration of the spiked sample (acetone solvent) in $\mu\text{g/L}$.

D - Concentration of the spiked sample (pentane solvent) in $\mu\text{g/L}$.

SECTION 7

METHOD DETECTION LIMITS FOR PHENOLS

INTRODUCTION

A study was performed to determine methods detection limits (MDL) for priority pollutant phenols included in the Environmental Protection Agency (EPA) Test Methods. The study was required because the previous practice was to determine the detection limits by either estimation or calculation based on a specific concentration giving a signal equivalent to a specific signal/noise ratio. A detection limit determined by these techniques may not actually be achievable for the compounds of interest in either water prepared in the laboratory or matrices encountered in environmental samples.

The EPA developed a method to determine the MDL, defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is greater than zero. Three sample matrices were used in the study for the MDL determination. Separate replicate sets of the three sample matrices were used to determine the MDL of the phenols by flame ionization gas chromatography (GC/FID) and the MDL by the derivative technique with analysis by electron capture gas chromatography (GC/EC).

Based on the determined method detection limits for each of the 11 phenols in interference-free water, analytical curves were established for both the GC/FID and GC/EC techniques.

EXPERIMENTAL

The MDL was determined for the phenols by both the GC/FID and GC/EC techniques, on interference-free water and two industrial wastewaters. The two wastewaters were from diverse sources:

- Sample DCA -- Effluent wastewater from a primary and secondary activated sludge treatment system followed by tertiary activated carbon treatment. Wastewater source is a large producer of inorganic and organic chemicals.
- Sample PBA-A -- Effluent wastewater from an industrial wastewater treatment plant, consisting of API oil/water separators, rapid sand filtering, and equalization tank, rotating biological contractors, and final clarifiers. The wastewater source is a Class B refinery producing gasoline, kerosene, jet fuel, heating oils, heavy fuels, and LPG.

Separate aliquots of all spiked samples were extracted, derivatized, and analyzed by electron capture gas chromatography (GC/EC). The sample preparation for all spiked aliquots included the sample clean up described in the test method (Appendix A).

Following the MDL determination, interference-free water was spiked at five different concentrations: 4, 7, 10, 100, and 1000 times the determined MDL. Duplicate samples were prepared and analyzed for each of the five concentrations. The results were used to establish analytical curves.

Method Detection Limits -- Interference-Free Water

Table 42 summarizes the recovery data obtained by GC/FID for each of the phenols from seven separate spiked aliquots of interference-free water. Included are the spike values, average recovered values, standard deviations, MDL values, and ratios of spikes to MDL values for each phenol.

Table 43 lists the actual recovered values obtained by the derivatization-GC/EC analysis steps of the test method. Also included are the spike values for the seven separate replicates, the average recovered values, standard deviation, MDL values, and spike to MDL ratios.

Analytical Curves -- Interference-Free Water

The analytical curves were separately determined for each of the phenols in the interference-free water by both GC/FID and derivatization-GC/EC.

For the GC/FID study, five duplicate one-liter samples of interference-free water were spiked with specific concentrations of the phenols. Except for 2,4-DNP, 4,6-DN-2MP, and PCP, the spiking concentrations of each compound represented approximately 4, 8, 10, 100, and 1000 times the MDL in interference-free water, as determined by GC/FID. The highest spiking concentration of 2,4-DNP, 4,6-DN-2-MP, and PCP represented a maximum of 250 times the established MDL. This limitation was dictated by solubility restrictions. The spiking concentrations are listed in Table 44.

The analytical curve data generated by GC/FID analyses for phenols in interference-free water are listed in Tables 45 through 48.

Five duplicate one-liter samples of interference-free water were also spiked with 9 phenols for the derivatization-GC/EC analytical curve study. Because it is difficult to reproducibly derivatize the dinitrophenols, they were excluded from this study. The spiking concentrations of the phenols

TABLE 42. MDL FOR PHENOLS: FLAME IONIZATION DETECTION IN INTERFERENCE-FREE WATER

Sample No.	2-CP	2-NP	ØOH	2,4-DMP	2,4-DCP	2,4,6-TCP	4-C, 3-MP	2,4-DNP	4,6-DN, 2-MP	PCP	4-NP
1	.608	.792	.302	.715	.861	.389	.700	17.0	20.5	12.8	5.0
2	.712	.744	.296	.636	.787	.676	.676	27.5	35.6	19.2	6.9
3	.409	.430	.225	.429	.508	.635	.412	24.4	32.0	17.8	6.9
4	.597	.692	.283	.618	.808	1.03	.606	17.6	29.6	18.9	7.1
5	.577	.523	.344	.524	.632	.874	.505	18.8	30.9	17.2	6.3
6	.465	.462	.325	.479	.623	.787	.454	25.6	35.7	19.9	7.3
7	.565	.523	.228	.510	.731	.797	.462	23.2	31.9	17.7	7.8
Method MDL Data											
Spiked Value (µg/L)	.744	.796	.764	.82	1.03	1.20	.70	28.7	34.6	21.0	15.4
Average Recovered (µg/L) (n=7)	.562	.595	.286	.559	.707	.741	.545	22.0	30.9	17.6	6.8
Standard Deviation	.099	.145	.045	.101	.125	.202	.115	4.2	5.1	2.3	0.9
MDL = 3.143 X Standard Deviation	.32	.45	.14	.312	.39	.64	.36	13.2	16.1	7.4	2.8
Ratio = Spike/MDL	2	2	5	3	3	2	2	2	2	3	5

All concentrations are actual recovered values of µg/L based on water.

TABLE 43. MDL FOR PHENOLS DERIVATIZATION/ELECTRON CAPTURE DETECTION IN INTERFERENCE-FREE WATER

Sample No.	Ø-OH	2,4-DMP	2-CP	4-C, 3-MP	2,4-DCP	2,4,6-TCP	2-NP	4-NP	PCP
1	2.35	1.39	1.89	3.60	2.00	1.79	1.83	1.90	1.96
2	2.09	1.88	2.32	4.80	2.52	2.17	1.91	1.48	2.24
3	2.15	1.65	1.94	4.56	2.21	2.25	2.28	1.46	2.31
4	1.74	1.30	1.78	5.34	1.96	2.07	1.72	1.21	2.52
5	2.29	1.42	1.89	4.12	2.01	2.19	2.00	1.45	2.50
6	2.20	1.40	1.87	4.09	1.97	2.12	2.01	1.26	2.29
7	3.90	1.41	1.77	4.67	1.91	1.81	2.41	1.73	2.36
Method MDL Data									
Spiked Value (µg/L)	5.22	2.39	2.57	5.82	2.52	2.68	2.45	2.60	2.52
Average Recovered (µg/L) (n=7)	2.39	1.49	1.92	4.45	2.08	2.06	2.02	1.45	2.31
Standard Deviation	.695	.200	.185	.568	.217	.185	.246	.222	.188
MDL = 3.143 X Standard Deviation	2.19	.628	.581	1.79	.682	.581	.772	.699	.590
Ratio = Spike/MDL	2	4	4	3	4	5	3	4	4

All concentrations are actual recovered values of µg/L based on water.

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TABLE 44. PHENOL CONCENTRATIONS IN WATER

Compound	4 X MDL ($\mu\text{g/L}$)	8 X MDL ($\mu\text{g/L}$)	10 X MDL ($\mu\text{g/L}$)	100 X MDL ($\mu\text{g/L}$)	1000 X MDL ($\mu\text{g/L}$)
2-CP	1.24	2.48	3.10	31.0	310
2-NP	1.79	3.58	4.47	44.7	447
ϕOH	0.67	0.94	1.34	13.4	134
2,4-DMP	1.23	2.46	3.07	30.7	307
2,4-DCP	1.65	3.30	4.13	41.3	413
2,4,6-TCP	2.39	4.78	5.97	59.7	597
4-C-3-MP	1.40	2.80	3.49	34.9	349
4-NP	11.1	22.2	27.7	277	2770
2,4-DNP*	32.3	61.4	123	323	3230
4,6-DN-2-MP*	40.3	64.4	129	403	4030
PCP*	31.8	44.5	89.0	318	1800

*Because of solubility restrictions the values do not represent 4, 8, 10, 100, and 1000 times the established MDL.

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TABLE 45. ANALYTICAL CURVE DATA: FLAME IONIZATION DETECTION OF 2-CHLOROPHENOL, 2-NITROPHENOL, AND PHENOL IN INTERFERENCE FREE-WATER

Spike μg/L	2-Chlorophenol			2-Nitrophenol			Phenol		
	Recovered μg/l	% Recovery	Spike μg/L	Recovered μg/L	% Recovery	Spike μg/L	Recovered μg/L	% Recovery	
1.24	0.78	62.9	1.79	1.16	64.8	0.67	0.29	43.3	
1.24	1.42	115	1.79	1.46	81.6	0.67	0.29	43.3	
2.48	1.72	69.4	3.58	2.61	72.9	0.94	0.45	47.9	
2.48	2.10	84.7	3.58	2.54	70.9	0.94	0.53	56.4	
3.10	1.93	62.3	4.47	2.78	62.2	1.34	0.56	41.8	
3.10	2.08	67.1	4.47	3.31	74.0	1.34	0.60	44.8	
31.0	20.1	64.8	44.7	31.0	69.4	13.4	5.62	41.9	
31.0	19.3	62.3	44.7	29.8	66.7	13.4	5.37	40.1	
310	163	52.6	447	278	62.2	134	54.3	40.5	
310	185	59.7	447	308	68.9	134	57.4	42.8	

TABLE 46. ANALYTICAL CURVE DATA: FLAME IONIZATION DETECTION OF 2,4-DIMETHYLPHENOL, 2,4-DICHLOROPHENOL, AND 2,4,6-TRICHLOROPHENOL IN INTERFERENCE-FREE WATER

2,4-Dimethylphenol				2,4-Dichlorophenol				2,4,6-Trichlorophenol			
Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L
1.23	0.65	52.8	1.65	1.24	75.2	2.39	1.73	2.39	1.73	72.4	2.39
1.23	0.73	59.3	1.65	1.40	84.8	2.39	1.92	2.39	1.92	80.3	2.39
2.46	1.51	61.4	3.30	2.36	71.5	4.78	3.73	4.78	3.73	78.0	4.78
2.46	1.58	64.2	3.30	2.50	75.8	4.78	3.96	4.78	3.96	82.8	4.78
3.07	2.01	65.5	4.13	3.02	73.1	5.97	4.14	5.97	4.14	69.3	5.97
3.07	2.28	74.3	4.13	3.43	83.1	5.97	4.86	5.97	4.86	81.4	5.97
30.7	20.5	66.8	41.3	30.6	74.1	59.7	49.8	59.7	49.8	83.4	59.7
30.7	23.1	75.2	41.3	29.3	70.9	59.7	48.7	59.7	48.7	81.6	59.7
307	226	73.6	413	304	73.6	597	529	597	529	88.6	597
307	236	76.9	413	325	78.7	597	565	597	565	95.1	597

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TABLE 47. ANALYTICAL CURVE DATA: FLAME IONIZATION DETECTION OF 4-CHLORO-3-METHYLPHENOL,
2,4-DINITROPHENOL, AND 4,6-DINITRO-2-METHYLPHENOL IN INTERFERENCE-FREE WATER

4-Chloro-3-methylphenol				2,4-Dinitrophenol				4,6-Dinitro-2-methylphenol			
Spike μg/L	Recovered μg/L	% Recovery	Spike μg/L	Recovered μg/L	% Recovery	Spike μg/L	Recovered μg/L	Spike μg/L	Recovered μg/L	% Recovery	Spike μg/L
1.40	0.93	66.4	32.3	19.8	61.3	40.3	30.7	40.3	30.7	76.2	40.3
1.40	1.08	77.1	32.3	22.0	68.1	40.3	37.6	40.3	37.6	93.3	40.3
2.80	2.13	76.1	61.4	39.8	64.8	64.4	51.5	64.4	51.5	80.0	64.4
2.80	2.10	75.0	61.4	54.7	89.1	64.4	62.7	64.4	62.7	97.4	64.4
3.49	2.47	70.8	122.8	93	75.7	129	138	129	138	107	129
3.49	2.84	81.4	122.8	97	79.0	129	123	129	123	95.3	129
34.9	29.2	83.7	323	263	81.4	403	391	403	391	97.0	403
34.9	29.8	82.5	323	214	66.3	403	375	403	375	93.1	403
349	325	93.1	3232	3077	95.2	4026	4036	4026	4036	100	4026
349	338	96.8	3232	3258	101	4026	4200	4026	4200	104	4026

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TABLE 48. ANALYTICAL CURVE DATA FLAME IONIZATION DETECTION OF
PENTACHLOROPHENOL AND 4-NITROPHENOL IN INTERFERENCE-FREE WATER

Pentachlorophenol			4-Nitrophenol		
Spike $\mu\text{g/L}$	Recovered $\mu\text{g/L}$	% Recovery	Spike $\mu\text{g/L}$	Recovered $\mu\text{g/L}$	% Recovery
31.8	22.4	70.4	11.1	2.82	25.4
31.8	27.5	86.5	11.1	4.17	37.6
44.5	31.8	71.5	22.2	7.94	35.8
44.5	38.1	85.6	22.2	8.60	38.7
89.0	84.9	95.4	27.7	9.01	32.5
89.0	78.7	88.4	27.7	9.20	33.2
318	287	90.3	277	107	38.6
318	275	86.5	277	107	38.6
1800	1837	102	2772	1276	46.0
1800	1908	106	2772	1224	44.2

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represented approximately 4, 7, 10, 100, and 1000 times the MDL previously determined in interference-free water by derivatization-GC/EC. The analytical curve data are reported in Tables 49 through 51.

Method Detection Limits -- Industrial Wastewaters

The MDLs for the phenols were determined by both GC/FID and derivatization-GC/EC in two wastewaters. The original spiking levels in each sample were determined from a combination of the results obtained for the MDL is interference-free water and the background analyses of the unspiked wastewaters. Tables 52 through 55 list the actual recovery values obtained by the two test method options for wastewater samples DCA and PBA-A.

DISCUSSION

The method detection limits (MDL) of the 11 phenols, as determined by GC/FID on interference-free water samples, are generally lower than the calculated MDLs (Table 56). Two exceptions were 2,4-dinitrophenol and 4,6-dinitro-2-methyl phenol. The MDLs for these compounds were approximately twice the calculated MDL. The higher values are believed to be due to chromatographic problems existing at the calculated MDL concentration. The ability of the 1% SP 1240 DA column to resolve 2,4-DNP from 4,6-DN-2-MP is limited at low concentrations. This resolution problem increases the standard deviation, which, in turn, increases the MDL value.

The MDLs established for interference-free water by the derivatization-GC/EC techniques are five to twenty times lower than the practical and calculated MDLs (Table 57).

The MDLs established for the phenols in the two wastewaters were generally higher than for those determined in interference-free water (Tables 58 and 57).

CONCLUSIONS AND RECOMMENDATIONS

The EPA method of determining the MDL appears to be satisfactory. However, the analyst should develop MDL, recovery, and precision data on the water type of concern.

The probability exists that in some cases MDLs lower than those determined in this study could be achieved. Some of the extraneous factors affecting the MDL determination are:

1. Lack of baseline separation - related to single versus multiple component solutions
2. "One of a kind" column
3. Peak broadening
4. Percent recovery
5. Analysts

Not all of the phenols and derivatives of phenols have baseline resolution from each other. Therefore, for compounds such as 2,4-DMP, 2,4-DCP,

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TABLE 49. ANALYTICAL CURVE DATA: DERIVATIZATION/ELECTRON CAPTURE DETECTION OF PHENOL, 2,4-DIMETHYLPHENOL, AND 2-CHLOROPHENOL IN REAGENT WATER

Phenol				2,4-Dimethylphenol				2-Chlorophenol			
Spike $\mu\text{g/L}$	Recovered $\mu\text{g/L}$	% Recovery	Spike $\mu\text{g/L}$	Recovered $\mu\text{g/L}$	% Recovery	Spike $\mu\text{g/L}$	Recovered $\mu\text{g/L}$	Spike $\mu\text{g/L}$	Recovered $\mu\text{g/L}$	% Recovery	Spike $\mu\text{g/L}$
8.66	3.50	40	3.10	2.52	81	2.23	1.49	2.23	1.49	67	2.23
8.66	3.03	35	3.10	2.26	73	2.23	1.28	2.23	1.28	57	2.23
15.2	6.05	40	5.43	4.37	80	3.91	2.74	3.91	2.74	50	3.91
15.2	5.13	34	5.43	4.15	76	3.91	2.28	5.58	2.28	58	5.58
21.6	7.90	37	7.76	5.09	66	5.58	2.89	5.58	2.89	52	5.58
21.6	8.33	38	7.76	6.04	78	5.58	3.63	55.8	3.63	65	55.8
216	96.3	45	77.6	68.1	88	55.8	43.3	55.8	43.3	78	55.8
216	91.1	42	77.6	70.3	91	55.8	40.0	55.8	40.0	72	55.8
2160	902	42	776	664	86	558	376	558	376	67	558
2160	985	46	776	751	97	558	469	558	469	84	558

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TABLE 50. ANALYTICAL CURVE DATA: DERIVATIZATION/ELECTRON CAPTURE DETECTION OF
4-CHLORO-3-METHYLPHENOL, 2,4-DICHLOROPHENOL, AND 2,4,6-TRICHLOROPHENOL IN REAGENT WATER

4-Chloro-3-methylphenol				2,4-Dichlorophenol				2,4,6-Trichlorophenol			
Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L	Recovered µg/L	Spike µg/L	Recovered µg/L	% Recovery	Spike µg/L
6.26	5.75	92	3.11	2.20	71	2.35	1.88	2.35	1.88	80	2.35
6.26	5.53	88	3.11	1.91	61	2.35	1.69	2.35	1.69	72	2.35
11.0	10.2	93	5.45	4.17	76	4.12	3.49	4.12	3.49	85	4.12
11.0	10.6	97	5.45	3.68	67	4.12	3.21	4.12	3.21	78	4.12
15.7	13.5	86	7.78	4.95	64	5.88	4.25	5.88	4.25	72	5.88
15.7	14.0	89	7.78	5.81	75	5.88	4.61	5.88	4.61	78	5.88
157	152	97	77.8	65.5	84	58.8	50.0	58.8	50.0	85	58.8
157	154	99	77.8	63.2	81	58.8	48.6	58.8	48.6	83	58.8
1570	1500	96	778	597	77	588	471	588	471	80	588
1570	1630	104	778	690	89	588	517	588	517	88	588

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TABLE 51. ANALYTICAL CURVE DATA: DERIVATIZATION/ELECTRON CAPTURE DETECTION OF
2-NITROPHENOL, 4-NITROPHENOL, AND PENTACHLOROPHENOL IN REAGENT WATER

2-Nitrophenol				4-Nitrophenol				Pentachlorophenol			
Spike μg/L	Recovered μg/L	% Recovery		Spike μg/L	Recovered μg/L	% Recovery		Spike μg/L	Recovered μg/L	% Recovery	
3.02	2.20	73		7.70	3.07	40		2.99	2.64	88	
3.02	1.90	63		7.70	3.45	45		2.99	2.53	85	
5.28	3.81	72		13.5	7.25	54		5.24	4.85	93	
5.28	3.51	67		13.5	9.77	72		5.24	5.78	110	
7.54	4.03	53		19.3	12.1	63		7.48	6.84	91	
7.54	5.39	71		19.3	12.8	66		7.48	6.81	91	
75.4	65.4	87		193	87.5	45		74.8	69.1	92	
75.4	67.3	89		193	92.4	48		74.8	68.2	91	
754	626	83		1930	956	50		748	655	88	
754	659	87		1930	1200	62		748	699	93	

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FIGURE 52. MDL DATA FOR PHENOLS: FLAME IONIZATION DETECTION IN WASTEWATER CODE DCA

Sample No.	2-CP	2-NP	ØOH	2,4-DMP	2,4-DCP	2,4,6-TCP	4-C,3-MP	2,4-DNP	4,6-DN,2-MP	PCP	4-NP
1	1.3	2.8	1.5	3.2	3.9	5.0	2.2	27.1	32.1	15.9	8.3
2	2.0	2.9	1.3	2.4	2.8	3.5	2.2	23.4	27.9	14.3	8.9
3	1.8	2.0	1.0	1.0	2.7	2.1	3.5	10.9	19.3	16.7	8.4
4	1.6	1.8	1.1	1.5	2.5	3.7	3.5	18.0	20.6	14.9	8.4
5	1.95	2.4	1.8	1.7	3.6	4.9	3.0	23.8	25.4	13.3	7.2
6	2.6	2.1	2.1	1.0	4.1	3.3	3.9	20.9	22.3	12.6	4.1
7	2.0	2.3	2.1	1.0	3.2	3.4	3.1	22.2	23.6	13.4	5.0
Method MDL Data											
Spiked Value (µg/L)	3.72	3.98	3.82	4.1	5.16	5.98	3.50	28.72	34.56	21.04	15.8
Average Recovered (µg/L) (n=7)	1.89	2.33	1.56	1.69	3.257	3.7	3.057	20.9	24.46	14.44	7.31
Standard Deviation	.403	.407	.454	.842	.624	.998	.6554	5.215	4.435	1.485	1.741
MDL = 3.143 X	1.27	1.28	1.43	2.645	1.962	3.138	2.06	16.39	13.94	4.67	5.47
Standard Deviation											
Ratio = Spike/MDL	3	3	3	2	3	2	2	2	3	5	3

All concentrations are actual recovered values of µg/L based on water.

TABLE 53. MDL DATA FOR PHENOLS: DERIVATIZATION/ELECTRON CAPTURE DETECTION IN WASTEWATER DCA

Sample No.	Ø-OH	2,4-DMP	2-CP	4-C, 3-MP	2,4-DCP	2,4,6-TCP	2-NP	4-NP	PCP
1	1.66	3.03	2.36	2.03	2.30	3.00	2.14	2.29	3.99
2	2.00	4.36	4.01	2.97	3.78	4.62	3.98	2.19	4.73
3	2.91	3.38	3.17	2.70	3.04	3.80	2.81	2.47	4.78
4	2.21	2.72	3.43	3.06	3.42	4.23	2.98	2.42	5.38
5	2.46	3.69	3.06	2.54	3.09	3.82	2.91	1.75	4.72
6	2.68	2.20	2.43	1.81	2.56	3.19	2.03	1.49	4.29
7	2.31	3.60	4.03	2.64	3.92	4.64	3.76	1.63	4.80
Method MDL Data									
Spiked Value (µg/L)	5.22	4.78	5.14	4.28	5.04	5.36	4.90	5.20	5.04
Average Recovered (µg/L) (n=7)	2.32	3.28	3.21	2.54	3.16	3.90	2.94	2.03	4.67
Standard Deviation	.419	.705	.673	.461	.598	.648	.734	.400	.437
MDL = 3.143 X Standard Deviation	1.32	2.22	2.12	1.45	1.88	2.04	2.31	1.26	1.37
Ratio = Spike/MDL	4	2	2	3	3	3	2	4	4

TABLE 54. MDL DATA FOR PHENOLS: FLAME IONIZATION DETECTION IN WASTEWATER CODE PBA-A

Sample No.	2-CP	2-NP	ØOH	2,4-DMP	2,4-DCP	2,4,6-TCP	4-C,3-MP	2,4-DNP	4,6-DN,2-MP	PCP	4-NP
1	2.2	2.4	1.8	1.9	4.7	5.9	2.7		36.0	16.9	6.8
2	1.9	2.6	1.5	1.9	4.7	5.7	2.6		32.7	16.4	8.1
3	2.2	2.6	2.1	1.4	4.2	4.9	3.1		30.0	17.3	5.9
4	2.5	2.3	1.5	1.6	5.5	5.98	2.7		36.8	18.1	8.2
5	3.6	3.3	1.9	2.0	5.3	5.5	3.2		36.6	18.2	7.8
6	3.7	2.8	1.9	1.9	4.4	4.8	2.9		37.1	20.7	7.35
7	2.6	2.7	1.5	1.7	4.4	4.95	2.8		31.6	16.1	6.5
Method MDL Data											
Spiked Value (µg/L)	3.72	3.98	3.82	4.10	5.16	5.98	3.50		34.56	21.04	15.88
Average Recovered (µg/L) (n=7)	2.7	2.7	1.7	1.8	4.7	5.4	2.86		34.4	17.7	7.2
Standard Deviation	.71	.33	.24	.21	.49	.5	.22		2.9	1.55	.87
MDL = 3.143 X Standard Deviation	2.2	1.02	.77	.67	1.5	1.6	.70		9.12	4.9	2.7
Ratio = Spike/MDL	2	4	6	6	3	4	5		4	4	6

All concentrations are actual recovered values of µg/L based on water.

TABLE 55. MDL DATA FOR PHENOLS: DERIVATIZATION/ELECTRON CAPTURE
DETECTION IN WASTEWATER PBA-A

Sample No.	Ø-OH	2,4-DMP	2-CP	4-C; 3-MP	2,4-DCP	2,4,6-TCP	2-NP	4-NP	PCP
1	2.26	2.81	3.74	1.99	3.68	4.54	3.61	1.91	4.12
2	2.13	2.39	4.13	2.34	4.09	4.68	3.69	1.86	4.56
3	2.25	1.91	3.52	2.13	3.52	4.29	3.32	1.80	4.35
4	1.92	2.54	4.28	2.45	4.19	4.79	3.22	1.79	4.08
5	1.62	1.90	3.69	2.22	3.59	4.41	3.15	1.95	3.95
6	2.00	2.11	4.66	2.68	4.52	5.25	3.30	1.95	4.73
7	2.68	1.97	4.05	2.29	4.05	4.79	3.72	2.32	4.04
Method MDL Data									
Spiked Value (µg/L)	5.22	4.78	5.14	4.28	5.04	5.36	4.90	5.20	5.04
Average Recovered (µg/L) (n=7)	2.12	2.23	4.01	2.30	3.95	4.68	3.43	1.94	4.26
Standard Deviation	.331	.354	.394	.224	.364	.316	.236	.180	.295
MDL = 3.143 X Standard Deviation	1.04	1.11	1.24	.705	1.15	.993	.743	.564	.928
Ratio = Spike/MDL	5	4	4	6	4	5	7	9	5

All concentrations are actual recovered values of µg/L based on water.

TABLE 56. COMPARISON OF TRUE MDL TO CALCULATED MDL FOR
PHENOLS FLAME IONIZATION DETECTION

Compound	True MDL ($\mu\text{g/L}$)	Calculated MDL ($\mu\text{g/L}$)
2-CP	0.31	2.0
2-NP	0.46	2.5
ϕOH	0.14	1.4
2,4-DMP	0.32	1.7
2,4-DCP	0.39	2.1
2,4,6-TCP	0.64	5.0
4-C-3-MP	0.36	8.3
2,4-DNP	13	7.0
2-M-4,6-DNP	16	10
PCP	7.4	10
4-NP	2.8	10

TABLE 57. COMPARISON OF TRUE MDL TO CALCULATED AND PRACTICAL MDL FOR PHENOLS DERIVATIZATION-GC/EC

Compound	True MDL ($\mu\text{g/L}$)	Calculated MDL ($\mu\text{g/L}$)	Practical MDL ($\mu\text{g/L}$)
ϕOH	2.19	14.8	10
DMP	0.63	3.2	10
2-CP	0.58	7.4	10
4-C1-3-MP	1.79	9.4	10
DCP	0.68	4.7	10
TCD	0.58	6.5	10
2-NP	0.77	6.4	10
4-NP	0.70	7.9	10
PCP	0.59	15	10
4,6-DN-2-MP	^a	100	30 ^b
2,4-DNP	^a	200	30 ^b

^aDerivative formation incomplete and irreproducible.

^bDetermined by GC/FID on underivatized extracts.

TABLE 58. COMPARISON OF METHOD DETECTION LIMITS FOR PHENOL (GC/FID)
IN THREE DIFFERENT MATRICES

Compound	Interference-Free Water ($\mu\text{g/L}$)	Industrial Wastewater Code DCA ($\mu\text{g/L}$)	Industrial Wastewater Code PEA ($\mu\text{g/L}$)
2-CP	0.311	1.27	2.20
2-NP	0.455	1.28	1.02
ϕOH	0.143	1.43	0.77
2,4-DMP	0.316	2.65	0.67
2,4-DCP	0.392	1.96	1.5
2,4,6-TCP	0.636	3.14	1.6
4-C-3-MP	0.362	2.06	0.70
2,4-DNP	13.2	16.4	Interference
4,6-DN-2-MP	16.1	13.9	9.12
PCP	7.4	4.67	4.9
4-NP	2.8	5.47	2.7

TABLE 59. COMPARISON OF METHOD DETECTION LIMITS FOR
PHENOLS (GC/EC) IN THREE DIFFERENT MATRICES

Compound	Interference-Free Water	Industrial Wastewater Code DCA ($\mu\text{g/L}$)	Industrial Wastewater Code PEA ($\mu\text{g/L}$)
2-CP	0.581	2.12	1.24
2-NP	0.772	2.31	0.743
ϕOH	2.19	1.32	1.04
2,4-DMP	0.628	2.22	1.11
2,4-DCP	0.682	1.88	1.15
2,4,6-TCP	0.581	2.04	0.993
4C-3-MP	1.79	1.45	0.705
PCP	0.590	1.37	0.928
4-NP	0.699	1.26	0.564

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and 4,6-DN-2MP, lower MDLs may be achieved by GC/FID or GC/EC, if the water is spiked with the individual compounds rather than by a mixture of all phenols.

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Compounds such as 2,4-DNP, 4,6-DN-2-MP, PCP, and 4-NP have less instrumental sensitivity than the other compounds because of peak broadening. This broadening occurs even when temperature programming is employed. If the analyst only determined a single compound, such as 4-NP, and isothermal GC conditions were possible, a lower MDL value may be achieved. The MDL of the phenols which elute at the higher temperatures are also affected by the increased background noise caused by the high temperature column bleed.

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APPENDIX A

PHENOLS: ANALYTICAL METHOD 604

1. Scope and Application

- 1.1 This method covers the determination of various phenolic compounds. The following parameters may be determined by this method:

<u>Parameter</u>	<u>STORET No.</u>	<u>Parameter</u>	<u>STORET No.</u>
4-Chloro-3-methyl-phenol	34452	2-Nitrophenol	34591
2-Chlorophenol	34586	4-Nitrophenol	34646
2,4-Dichlorophenol	34601	Pentachlorophenol	39094
2,4-Dimethylphenol	34606	Phenol	34694
4,6-Dinitro-2-methyl-phenol	34657	2,4,6-Trichloro-phenol	34621
2,4-Dinitrophenol	34616		

- 1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.
- 1.3 The sensitivity of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters with a flame ionization detector in the absence of interferences. If derivatization clean up is required, the sensitivity of the method is 10 µg/L. This concentration represents the minimum amount proven to date to give reproducible and linear response during derivatization.
- 1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

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2. Summary of Method

- 2.1 A 1 liter sample of wastewater is acidified and extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 mL or less. Flame ionization gas chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.
- 2.2 The method also provides for the preparation of pentafluorobenzyl bromide (PFBB) derivatives for electron capture gas chromatography with additional clean up procedures to aid the analyst in the elimination of interferences.

3. Interferences

- 3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be required.
- 3.2 Interferences coextracted from the samples will vary considerably from source to source, depending on the diversity of the industrial complex or municipality being sampled. While general clean up techniques are provided as part of this method, unique samples may require additional clean up approaches to achieve the sensitivities stated in Table A-1

4. Apparatus and Materials

- 4.1 Sampling equipment, for discrete or composite sampling.
- 4.1.1 Grab sample bottle - Amber glass, 1 liter or 1 quart volume. French or Boston Round design is recommended. The container must be washed and rinsed with solvent before use to minimize interferences.
- 4.1.2 Bottle caps - Threaded to screw on sample bottles. Caps must be lined with Teflon.
- 4.1.3 Compositing equipment - Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing or fittings may be used in this system.
- 4.2 Separatory funnel - 2000 mL, with Teflon stopcock.

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TABLE A-1. FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS

Compounds ^a	Retention Time (Minutes)	Detection Limit (µg/L) ^b
2-Chlorophenol	2.29	2.0
2-Nitrophenol	2.83	2.5
Phenol	3.71	1.4
2,4-Dimethylphenol	4.82	1.7
2,4-Dichlorophenol	5.10	2.1
2,4,6-Trichlorophenol	7.16	5.0
4-Chloro-3-methylphenol	8.55	8.3
2,4-Dinitrophenol	11.57	7.0
4,6-Dinitro-2-methylphenol	11.88	10.0
Pentachlorophenol	13.64	10.0
4-Nitrophenol	22.41	10.0

^aColumn conditions: Supelcoport 100/120 mesh coated with 1% SP-1240 DA in 6 ft long X 2 mm ID glass column with nitrogen carrier gas at 30 mL/min flow rate. Column temperature is 100°C at injection, programmed immediately at 8°C/min to 180°C final temperature.

^bDetection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 mL final extract volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

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4.3 Drying column - 20 mm ID Pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) apparatus

4.4.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask - 500 mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column - two ball micro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column - two ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips - solvent extracted, approximately 10/40 mesh.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 2^{\circ}\text{C}$). The bath should be used in a hood.

4.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on column injection and all required accessories including both flame ionization and electron capture detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column - 10 mm ID by 100 mm length, with Teflon stopcock.

4.8 Reaction vial - 20 mL with Teflon-lined cap.

5. Reagents

5.1 Preservatives

5.1.1 Sodium hydroxide - (ASC) 10 N in distilled water.

5.1.2 Sulfuric acid - (1 + 1) Mix equal volumes of conc. H_2SO_4 (ACS) with distilled water.

5.1.3 Sodium thiosulfate - (ACS) granular.

5.2 Methylene chloride, acetone, 2-propanol, hexane, toluene - Pesticide quality or equivalent.

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- 5.3 Sodium sulfate - (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hr in a shallow tray).
- 5.4 Stock standards - Prepare stock standard solutions at a concentration of 1.00 µg/µL by dissolving 0.100 grams of assayed reference material in pesticide quality 2-propanol and diluting to volume in a 100 mL ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just before preparing working standards from them.
- 5.5 Sulfuric acid - (ACS) 1 N in distilled water.
- 5.6 Potassium carbonate - (ACS) powdered.
- 5.7 Pentafluorobenzyl bromide (a-bromopentafluorotoluene) - 97% minimum purity.
- 5.8 1,4,7,10,13,16 - Hexaoxacyclooctadecant (18 crown 6) - 98% minimum purity.
- 5.9 Derivatization reagent - Add 1 mL pentafluorobenzyl bromide and 1 gram 18 crown 6 to a 50 mL volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly.
- 5.10 Silica gel - (ACS) 100/200 mesh, grade 923; activated at 130°C and stored in a desiccator.

6. Calibration

- 6.1 Prepare calibration standards for the flame ionization detector that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table A-1 as 100 µg/L in the final extract, for example, prepare standards at 10 µg/L, 50 µg/L, 100 µg/L, 500 µg/L, etc. so that injections of 1 to 5 µL of each calibration standard will define the linearity of the detector in the working range.
- 6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table A-1. By injecting calibration standards, establish the sensitivity limit of the detector and linear range of the analytical system for each compound.
- 6.3 Before using the derivatization clean up procedure, the analyst must process a series of calibration standards through the procedure to validate the precision of the derivatization and the absence of interferences from the reagents.

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7. Quality Control

- 7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are free from interference. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.
- 7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. Sample Collection, Preservation, and Handling

- 8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.
- 8.2 The samples must be iced or refrigerated from the time of collection until extraction. At the sampling location fill the glass container with sample. Add 35 mg sodium thiosulfate per part per million free chlorine per liter. Adjust the sample pH to approximately 2, as measured by pH paper, using appropriate sulfuric acid solution or 10 N sodium hydroxide. Record the volume of acid used on the sample identification tag so the sample volume can be corrected later.
- 8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. Sample Extraction

- 9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two liter separatory funnel. Adjust the sample pH to 12 with sodium hydroxide.
- 9.2 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for one minute with periodic venting to release vapor pressure. Allow the organic layer to separate from the water

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phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends on the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Discard the methylene chloride layer, and wash the sample with an additional two 60 mL portions of methylene chloride in similar fashion.

- 9.3 Adjust the aqueous layer to a pH of 1 to 2 with sulfuric acid.
- 9.4 Add 60 mL methylene chloride to the sample and shake for two minutes. Allow the solvent to separate from the sample and collect the methylene chloride in a 250 mL Erlenmeyer flask.
- 9.5 Add a second 60 mL volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.
- 9.6 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3 to 4 inches of anhydrous sodium sulfate, and collect it in a 500 mL Kuderna-Danish (K-D) flask equipped with a 10 mL concentrator tube. Rinse the Erlenmeyer flask and column with 20 to 30 mL methylene chloride to complete the quantitative transfer.
- 9.7 Add 1 to 2 clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a steaming hot (60 to 65°C) water bath so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.
- 9.8 Increase the temperature of the hot water bath to 95 to 100°C. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of 2-propanol. A 5-mL syringe is recommended for this operation. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of 2-propanol to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 2.5 mL, remove the K-D apparatus

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and allow it to drain for at least 10 minutes while cooling. Add an additional 2 mL of 2-propanol through the top of the micro-Snyder column and resume concentrating as before. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of 2-propanol. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store in refrigerator if further processing will not be performed immediately. If the sample extract requires no further clean up, proceed with flame ionization gas chromatographic analysis. If the sample requires clean up, proceed to Section 11.

- 9.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. After correction for sulfuric acid preservative, record the sample volume to the nearest 5 mL.

10. Gas Chromatography - Flame Ionization Detector

- 10.1 Table A-1 summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by one of these columns is shown in Figure A-1. Calibrate the gas chromatographic system daily with a minimum of three injections of calibration standards.
- 10.2 Inject 2 to 5 mL of the sample extract using the solvent flush technique. Smaller (1.0 mL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μ L, and the resulting peak size, in area units.
- 10.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.
- 10.4 If the peak area measurement is prevented by the presence of interferences, the phenols must be derivatized and analyzed by electron capture gas chromatography.

11. Derivatization and Electron Capture Gas Chromatography

- 11.1 Pipet a 1.0 mL aliquot of the 2-propanol solution of standard or sample extract into a glass reaction vial. Add 1.0 mL derivatization reagent. This is a sufficient amount of reagent to derivatize a solution whose total phenolic content does not exceed 0.3 mg/mL.
- 11.2 Add about 3 mg potassium carbonate to the solution and shake gently.

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COLUMN: 1% SP-1240DA on Supelcoport
PROGRAM: 80°C.-0 Minutes 8°/Minute to 150°C
DIRECTOR: Flame Ionization

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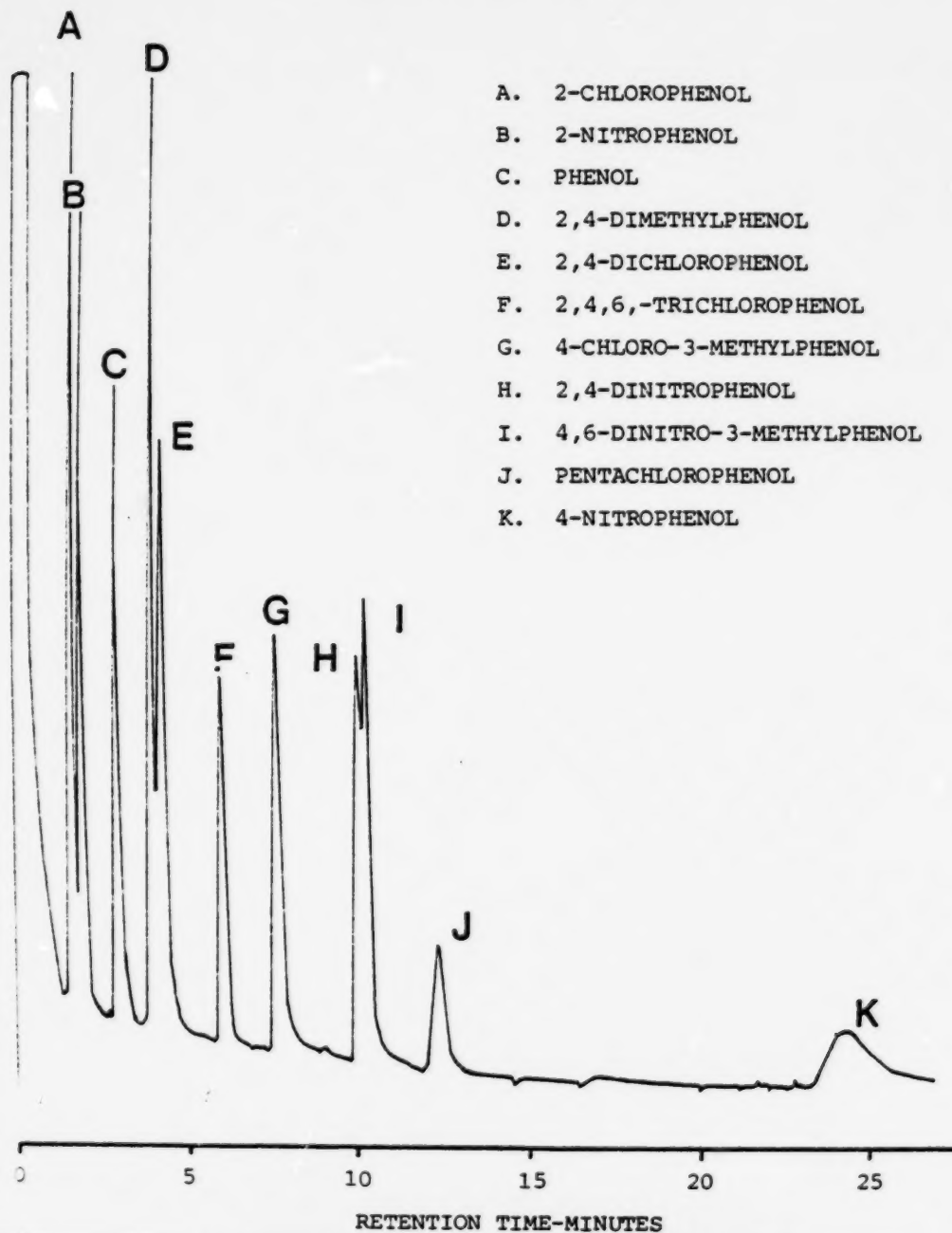


Figure A-1. Gas chromatogram of Phenols

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- 11.3 Cap the mixture and heat it for 4 hours at 80°C in a hot water bath.
- 11.4 Remove the solution from the hot water bath and allow it to cool.
- 11.5 Add 10 mL hexane to the reaction vial and shake vigorously for one minute. Add 3.0 mL distilled, deionized water to the reaction vial and shake for two minutes.
- 11.6 Decant organic layer into a concentrator tube and cap with a glass stopper.
- 11.7 Pack a 10 mm ID chromatographic column with 4.0 grams of activated silica gel. After settling the silica gel by tapping the column, add about 2.0 grams of anhydrous sodium sulfate to the top.
- 11.8 Pre-elute the column with 6 mL hexane. Discard the eluate and just before exposure of the sulfate layer to air, pipet onto the column 2.0 mL of the hexane solution (11.6) that contains the derivatized sample or standard. Elute the column with 10.0 mL hexane (Fraction 1) and discard this fraction. Elute the column, in order, with: 10.0 mL 15% toluene in hexane (Fraction 2); 10.0 mL 40% toluene in hexane (Fraction 3); 10.0 mL 75% toluene in hexane (Fraction 4); and 10.0 mL 15% propanol in toluene (Fraction 5). Elution patterns for the phenolic derivatives are shown in Table A-2. Fractions may be combined as desired, depending on the specific phenols of interest or level of interferences.
- 11.9 Analyze the fractions by electron capture gas chromatography. Table A-2 summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separation achieved by this column are shown in Figure A-2. Calibrate the system daily with a minimum of three aliquots of calibration standards, containing each of the phenols of interest that are derivatized according to the procedure.
- 11.10 Inject 2 to 5 μL of the column fractions using the solvent-flush technique. Smaller (1.0 μL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL , and the resulting peak size, in area units. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

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TABLE A-2. ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFBB DERIVATIVES

Parent Compound ^a	Retention Time (minutes)	Recovery Percent by Fraction				
		1	2	3	4	5
2-Chlorophenol	3.5			90	>1	90
2-Nitrophenol	9.5				9	
Phenol	2.0			90	10	
2,4-Dimethylphenol	3.0			95	7	
2,4-Dichlorophenol	6.0			95	>1	
2,4,6-Trichlorophenol	7.3		50	50		
4-Chloro-3-methylphenol	5.0			84	14	
Pentachlorophenol	29.7		75	20		
4-Nitrophenol	14.5				>1	
(2,4-Dinitrophenol)	46.9					
(2-Methyl-4,6-dinitrophenol)	36.6					

^aColumn conditions: Chromosorb W-AW-DMCS 80/100 mesh coated with 5% OV-17 packed in a 1.8 m long X 2.0 mm ID glass column with 5% methane/95% argon carrier gas at 30 mL/min flow rate. Column temperature is 200°C.

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COLUMN: 5% OV-17 on Chromosorb W-AW

TEMPERATURE: 200°C

DETECTOR: Electron Capture

- A. PHENOL
- B. 2,4-DIMETHYLPHENOL
- C. 2-CHLOROPHENOL
- D. 4-CHLORO-3-METHYLPHENOL
- E. 2,4-DICHLOROPHENOL
- F. 2,4,6-TRICHLOROPHENOL
- G. 2-NITROPHENOL
- H. 4-NITROPHENOL
- I. PENTACHLOROPHENOL

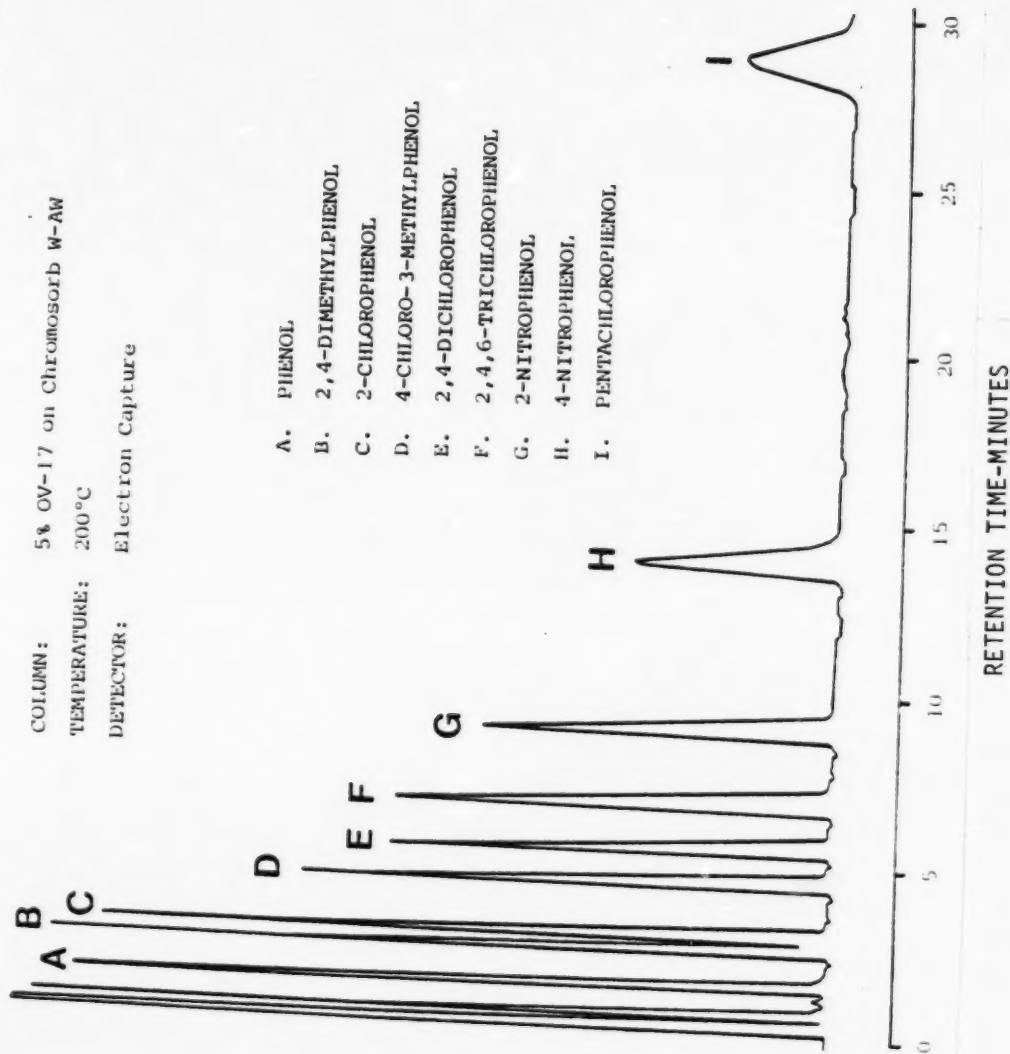


Figure A-2. Gas Chromatogram of PFBB Derivatives of Phenols

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12. Calculations

- 12.1 Determine the concentration of individual compounds measured by the flame ionization procedure (without derivatization) according to the formula:

$$\text{Concentration, } \mu\text{g/L} = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where: A = Calibration factor for chromatographic system, in nanograms material per area unit

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (μL)

V_t = Volume of total extract (μL)

V_s = Volume of water extracted (mL)

- 12.2 Determine the concentration of individual compounds measured by the derivatization and electron capture method according to the following procedure.

12.2.1 From the concentration of the calibration standards that were derivatized with the samples, calculate the amounts in nanograms of underivatized phenols that were added as 2-propanol solution (11.1). From the size of the injection into the electron capture gas chromatograph, determine the nanograms of material (calculated as the underivatized phenol) injected onto the column. Compare the detector responses obtained to develop a calibration factor for the chromatographic system, in nanograms of material per area unit.

- 12.2.2 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu\text{g/L} = \frac{(A)(B)(V_t)(10)(D)}{(V_i)(V_s)(C)(E)}$$

Where: A = Calibration factor for chromatographic system, in nanograms material per area unit, calculated as underivatized phenol

B = Peak size in injection of sample extract, in area units

V_i = Volume of eluate injected (μL)

V_t = Total volume of column eluate (μL)

V_s = Volume of water extracted (mL)

C = Volume of hexane sample solution added to clean up column, in mL

D = Total volume of 2-propanol extract after concentration

E = Volume of 2-propanol extract used for derivatization

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12.3 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. Accuracy and Precision

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The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of the test procedure.

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GLOSSARY OF TERMS

The terminology and statistical measurements used in this study report are defined as follows:

Accuracy as % Relative Error (Bias). The signed difference between mean value and the true value, expressed as a percent of the true value.

$$R. E., \% = \frac{\bar{X} - X_{true}}{X_{true}} \times 100$$

F-tests A statistical test applied to the ratio of the squares of S and/or S_r data to estimate whether the water types used in the study were statistically different than the distilled water data.

The following formulae (4) were used:

$$F = \frac{(S \text{ Distilled Water})^2}{(S \text{ Any Other Water Type})^2}$$

$$F = \frac{(S_r \text{ Distilled Water})^2}{(S_r \text{ Any Other Water Type})^2}$$

To achieve a number greater than 1 the variances were reversed as needed. The resultant values were compared to a standard one-sided 99.5% critical value table (5) to determine deviation where:

f (degrees of freedom) = n - 1

f' (degrees of freedom = n' - 1

n = number of data points to calculate the S or S_r in the numerator;

n' = number of data points to calculate the S or S_r in the denominator.

If the calculated F exceeds the theoretical value found in the table, the data may be considered significantly different.

Mean Recovery. The arithmetic mean of reported values; the average.

$$\bar{X} = \frac{\sum X_i}{n}$$

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Median. Middle value of all data ranked in ascending order. If there are two middle values, the mean of these values.

n. The number values (X_i) reported for a sample.

Non-Dechlorinated Finished Drinking Water. Water taken from the laboratory water tap and spiked for analysis without addition of sodium thiosulfate.

Outlier. A datum point determined by applying an Extreme Studentized Deviate T test at a selected probability level to be extreme in relationship to the other data and therefore rejected.

Range. The difference between the lowest and highest values reported for a sample.

Relative Deviation (Coefficient of Variation). The ratio of the standard deviation, S , of a set of numbers to their mean, $\bar{X}$, expressed as percent. It is an attempt to relate deviation (precision) of a set of data to the size of the numbers so that deviations at different mean values can be compared.

$$R. D. = 100 \frac{S}{\bar{X}}$$

Single-Analyst Relative Deviation. The ratio of the single-analyst standard deviation, S_r , of a set of numbers to their mean, $\bar{X}$, expressed as percent. It is an attempt to relate deviation (precision) of a set of data for a single analyst to the size of numbers so that the deviations at different mean values and between analysts can be compared.

$$\text{Single-analyst R.D.} = 100 \frac{S_r}{\bar{X}}$$

Standard Deviation (S). The most widely used measure to describe the dispersion of a set of data. For normally distributed data, $\bar{X} + S$ will include 68%, and $\bar{X} + 2S$ will include about 95% of the data from a study.

$$S = \sqrt{\frac{\sum (X_i - \bar{X})^2}{n - 1}}$$

Standard Deviation: Single Analyst (S_r). A measure of dispersion for data from a single analyst. Calculated here using an equation developed by Youden based on his nonreplicate study design.

$$S_r = \sqrt{\frac{\sum (D_i - \bar{D})^2}{2(n - 1)}}$$

Student's t-test. A statistical test performed to determine whether the mean recoveries, $\bar{X}$, for a particular water type when compared to distilled

water data were significantly different. The calculated t values were compared to a standard two-tailed t distribution table (5); calculated values exceeding the table values were considered significantly different.

When S_r values were found to be similar the following t-test was used:

$$t = \frac{\bar{X} - \bar{Y}}{\sqrt{n_x S_x^2 + n_y S_y^2}} \sqrt{\frac{n_x n_y (n_x + n_y - 2)}{n_x + n_y}}$$

which will have student t's distribution with $n_x + n_y - 2$ degrees of freedom.

Where:

$\bar{X}$ = the larger of the mean recoveries (water type or distilled water);

$\bar{Y}$ = the smaller of the mean recoveries (water type or distilled water);

n_x and n_y = the corresponding number of data points for $\bar{X}$ and $\bar{Y}$;

S_x^2 and S_y^2 = the corresponding S_r , single-analyst standard deviations for $\bar{X}$ and $\bar{Y}$.

When S_r values were found to be significantly different the following formulas were applied:

$$t = \frac{\bar{X} - \bar{Y}}{\sqrt{\frac{S_x^2}{n_x} + \frac{S_y^2}{n_y}}}$$

Where the degrees of freedom were:

$$= \frac{\left(\frac{S_x^2}{n_x} + \frac{S_y^2}{n_y} \right)^2}{\left(\frac{S_x^2}{n_x} \right)^2 \frac{1}{n_x + 1} + \left(\frac{S_y^2}{n_y} \right)^2 \frac{1}{n_y + 1}} - 2$$

T test. The difference between a single observation (X_0) and the estimated population mean ($\bar{X}$) expressed as a ratio over the estimated population standard deviation (S). The value obtained is compared with values from a table for the critical T distribution (3). If the calculated T value exceeds the theoretical T value at a prescribed confidence level, the analyzed value is probably not from the same population as the rest of the data and can be rejected.

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$$T = \frac{x_n - \bar{x}}{S}$$

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Youden Pair. A set of two samples having slightly dissimilar concentrations of the constituent of concern, based on Youden's nonreplicate analysis technique.

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APPENDIX B

A-26 RESIN/GC-FID METHOD FOR PHENOLS

SUMMARY

The method given here is that reported by Chriswell *et al.* (1). Phenols are trapped (as phenolate anions) on A-26 anion exchange resin by passing alkaline sample through a column of resin in the hydroxyl form. Any neutral organic compounds retained by the resin are washed off with alkaline methanol. The column is then washed with aqueous hydrochloric acid to convert the phenolate anions back to the acid form and elute them from the column. The elution is completed with an acetone-water solution and all eluates extracted with methylene chloride for gas chromatography with flame ionization detection (FID).

For other methods used for phenol analysis, see Procedure Codes No. 7 and No. 15.

INTERFERENCES

- 2.1 Solvents, reagents, glassware, and other sample-processing hardware may yield discrete artifacts and/or elevated baselines that could cause misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.
- 2.2 Common inorganic ions and many organic substances cause no interference, and neutral organics that are retained by the resin can be removed by a methanol wash.
- 2.3 The interferences in industrial effluents are many and varied, and often pose great difficulty in obtaining accurate and precise measurement of phenols. Sample clean-up procedures are generally required and may result in the loss of certain phenols. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all the interferences that may be encountered in industrial effluents.

APPARATUS AND MATERIALS

- 3.1 Gas Chromatograph - equipped with dual flame ionization detectors.

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3.2 Recorder - Potentiometric strip chart (10 inch) compatible with the detectors.

3.3 Gas Chromatographic Column Materials - see method variations.

3.4 Detector Options

3.4.1 Dual flame ionization

3.4.2 Electron capture - radioactive (tritium or nickel 63) - if phenols of interest are halogenated.

3.5 Kuderna-Danish (K-D) Glassware

3.5.1 Synder column - three ball (macro) and two ball (micro)

3.5.2 Evaporative flasks - 500 ml

3.5.3 Receiver ampules - 10 ml, graduated

3.5.4 Ampule stoppers

3.6 Chromatographic column - 1/2 in X 6 in glass chromatographic column with a 1,000 ml reservoir and a coarse fritted plate on bottom, prepared by pouring a water slurry of the cleaned A-26 resin into the column until the resin bed is within about one-half inch of the top of the column. The column is placed in the hydroxy form by passing approximately 20 ml of 0.1 M sodium hydroxide solution through the resin. Excess sodium hydroxide is washed from the resin bed with 50 ml of purified distilled water. Verify that there was excess hydroxide on the column by testing the first portion of water wash with pH paper (color should indicate pH >9).

3.7 Filter - medium porosity, 150 ml sintered glass filter

3.8 Separatory funnels - 125 ml with Teflon stopcock

3.9 Graduated cylinders - 50 ml, 100 ml and 500 ml

3.10 Porous polymer resin - Rohm & Haas A-26 anion exchange resin screened to remove beads smaller than 60 mesh. Clean new resin by placing in a sintered glass filter attached to a suction flask, washing successively with 2 M sodium hydroxide, purified distilled water, 4 M hydrochloric acid, purified distilled water and acetone. Repeat sequence of washings until no color is apparent in the final acetone wash (generally one to three times). Then extract with acetone for 24 hours in a Soxhlet extractor.

REAGENTS, SOLVENTS AND STANDARDS

4.1 Sodium hydroxide - (ACS)

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4.1.1 2 M solution in distilled water

4.1.2 0.1 M solution in distilled water

4.2 Hydrochloric acid - (ACS) 4 M solution in distilled water

4.3 Acetone, methylene chloride, methanol-nanograde, redistilled in glass if necessary.

4.4 Hydroxylamine hydrochloride - ACS

4.5 Sodium hydrosulfite - ACS

4.6 Phenol - compound(s) being analyzed

QUALITY CONTROL

5.1 Standards should be injected frequently, as a check on the stability of the operating conditions.

5.2 Duplicate and spiked sample analyses are recommended as quality control checks. When the routine occurrence of a phenol is being observed, the use of quality control charts is recommended.

5.3 Each time a set of samples is extracted, a method blank is determined in a volume of distilled water equivalent to that used to dilute the sample.

SAMPLE PREPARATION

6.1 Take a 500 ml sample of water. If phenol standards are added to water containing chlorine, add 15 to 25 mg of hydroxylamine hydrochloride and allow to stir for at least 5 minutes before proceeding. Add 15 to 25 mg of sodium hydrosulfite to the sample, and adjust the pH to between 12.0 and 12.5 with 2 M sodium hydroxide.

6.2 If a precipitate forms, coagulate it by allowing the sample to sit for about 15 minutes. Decant the supernatant liquid through a medium-porosity, 150 ml sintered-glass filter attached to a suction flask. Wash the precipitate into the filter with a minimum amount of water, then wash thoroughly with approximately 50 ml of distilled water.

6.3 Pour the filtered water and washings into the reservoir of the adsorption column and allow to flow through the resin column at a rate of 10 to 15 ml/min.* When the liquid level reaches the top of the resin bed, wash the column with 25 ml of basic methanol (2 ml of 2 M sodium hydroxide in 23 ml of methanol) and 25 ml of distilled water.

6.4 Place a 125-ml separatory funnel under the column, and elute the column with 25 ml of 4 M hydrochloric acid, then with 25 ml of distilled water. (The first portion of water should test acidic to pH

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paper.) Extract the solution in the separatory funnel with 25 ml of methylene chloride. Allow the phases to separate and become clear; then drain the lower methylene chloride layer into a second 125-ml separatory funnel and discard the aqueous layer.

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Some workers have found better phenolate exchange when a slower flow rate is used (about 3 ml/min) in this step (see Variation No. 2).

- 6.5 Elute the column with 60 ml of 5:1 (V:V) acetone:water and 50 ml of distilled water in sequence into the separatory funnel containing the methylene chloride. Shake, allow the phases to separate and clear; then drain the lower organic layer into a K-D evaporating flask.
- 6.6 Add a small boiling chip to the flask, attach a Snyder column, and evaporate the solvent over a steam bath until the volume is reduced to approximately 0.5 ml. Remove the evaporating flask from the steam, and immediately spray the outside with acetone to condense the vapors inside. Adjust the volume to exactly 1.0 ml with acetone.
- 6.7 Inject 2 μ l of the acetone solution into the gas chromatograph (see GC conditions, below).

Note: If the acetone solvent peak interferes with some of the individual phenol peaks, the acetone may be removed by adding approximately 7 ml of pentane to the evaporated (1.0 ml) acetone extract. By evaporating and diluting to exactly 1.0 ml with pentane, the acetone is volatilized by azeotropic distillation. Injection of a pentane solution permits operation of the gas chromatograph at significantly lower attenuation settings without interference from a tailing edge of the solvent peak.

CALCULATION OF RESULTS

- 7.1 Determine the phenol concentration by comparing either peak heights or areas against a previously prepared calibration curve.

REPORTING RESULTS

- 8.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained must be reported on the analytical quality control report sheets.

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Variation
Code No.

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Description

1

June 1977

GC Column: 1% SP-1240 DA on 100/120 mesh Supelcoport in a 4 ft X 2 mm ID glass column.

Temperature: 80°C to 180°C at 10°/min, hold at 180°C for 15 min

Injector: 240°C

Detector: FID at 240°C

Carrier: He at 35 ml/min

(Source: Envirodyne Engineers, Inc.)

2

February 1979

Same as Variation 1, except Column

Temperature: 80° for 5 min, 80° to 180° at 10°/min, hold at 180° for 15 min

3

June 17

A. 3 ml/min flow rate for initial phenolate anion exchange (Step 6.3); regenerate resin with 2 M NaOH instead of 0.1 M NaOH.

B. GC column: 1% SP-1240 DA on Supelcoport (100.120 mesh) in a 6' X 2 mm ID glass column

Temperature: 4 min at 85°C then 10°/min to 200°C

Injector: 180°C

Detector: FID at 200°C

Carrier: N₂ at 30 ml/min

(Source: Midwest Research Institute)

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May 1979

Same as Variation 1, except as follows:

Column Temperature: 80°C for 10 min,
increase to 180°
at 5°/min, hold at
180° for 30 min

Injector: 190°C

Detector: FID at 300°C

Carrier: He at 35 ml/min

(Source: EEI)

5

May 1979

Same as Variation 1, except as follows:

Column Temperature: 80°C for 13 min,
increase to 180°C
at 10°/min and
hold at 180°C
for 30 min

REFERENCES.

1. Christwell, C. D., Cheng, R. C., and Fritz, J. S., "Chromatographic Determination of Phenols in Water," Anal. Chem. 47, 1325-1329 (1975).

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